159. Glycosylidene Carbenes

Part 2

Synthesis of *O*-Aryl Glycosides

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Phenol, 4-methoxyphenol, 4-nitrophenol, methyl orsellinate (**1**), and 2,6-di(*tert*-butyl)-4-methylphenol (BHT; **2**) have been glycosylated by thermal reaction (20–60°) with various glycosylidene-derived diazirines.

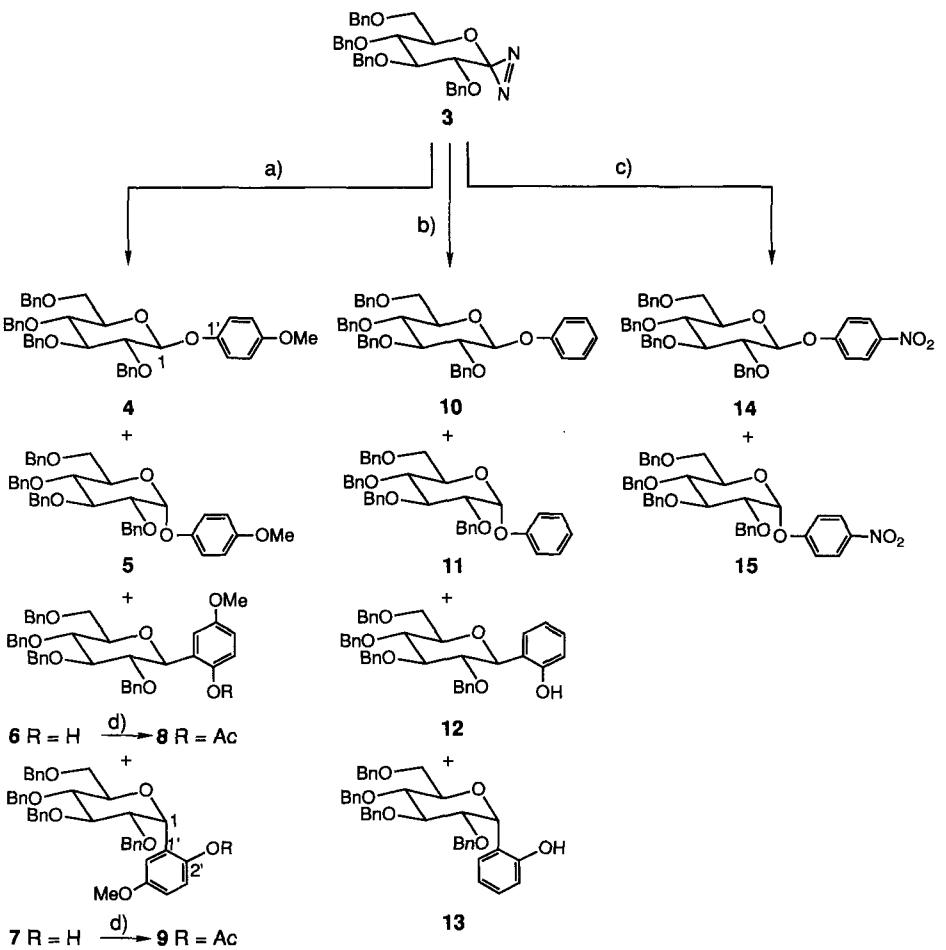
4-Methoxyphenol reacted with the D-glucosylidene-derived diazirine **3** to give *O*-glucosides (**4** and **5**, 69%, 3:1) and *C*-glucosides (**6** and **7**, 16%, 1:1). Similarly, phenol yielded *O*-glucosides (**10** and **11**, 70%, 4:1) and *C*-glucosides (**12** and **13**, 13%, 1:1). 4-Nitrophenol gave only *O*-glycosides, **3** leading to **14** and **15** (75%, 3:2; *Scheme 1*), and the D-galactosylidene-derived diazirine **17** to **22** and **23** (52% (from **16**), 65:35; *Scheme 2*). The reaction of phenol with **17** yielded 58% (from **16**) of the *O*-galactosides **18** and **19** (4:1) and 14% of the *C*-galactosides **20** and **21** (1:1). From the D-mannosylidene-derived diazirine **25**, we predominantly obtained the α-D-configurated **26** (38% from **24**). These results are interpreted by assuming that an intermediate (presumably a glycosylidene carbene) first deprotonates the phenol to generate an ion pair which combines to give *O*- and – with electron-rich phenolates – also *C*-glycosides. A competition experiment of **3** with 4-nitro- and 4-methoxyphenol gave the products from the former (**14** and **15**) and the latter phenol (**4**–**7**) in almost equal amounts. Differences in the *kinetic* acidity of OH groups, however, may form the basis of a regioselective glycosidation, as evidenced by the reaction of **3** with methyl orsellinate (**1**) yielding exclusively the 4-*O*-monoglycosylated products **27** and **28** (78%, 85:15), although diglycosidation is possible (**27** → **31** and **32**; 67%, 4:3; *Scheme 3*). Steric hindrance does not affect this type of glycosidation; **3** reacted with the hindered BHT (**2**) to afford **33** and **34** (81%, 4:1). The predominant formation of 1,2-*trans*-configurated *O*-aryl glycosides is rationalized by a neighbouring-group participation of the 2-benzyloxy group.

Introduction. – We have introduced glycosylidene-derived diazirines as precursors of glycosylidene carbenes and as glycosyl donors in a new method for the synthesis of glycosides which does not require a promoter [1]. We now report on the synthesis of *O*-aryl glycosides from these diazirines. *O*-Aryl glycosides are widespread in nature [2] and possess a variety of biological activities. Some are cytotoxic [3] or antiviral agents [4], others are used in the determination of the activity of glycosidases (see *e.g.* [5]). The synthesis of these glycosides has been studied extensively [6–13].

We have studied the glycosidation of 4-nitrophenol, phenol, 4-methoxyphenol, methyl orsellinate (**1**) [14], and 2,6-di(*tert*-butyl)-4-methylphenol (**2**) using the diazirines **3**, **17**, and **25**, derived from the *O*-benzylated D-*gluco*-, D-*galacto*-, and D-*manno*-hexopyranoses. These phenols were chosen to elucidate the influence of the acidity of phenols on the yields, the diastereoselectivity, and the regioselectivity of their glycosidation and to examine the dependency of the glycosidation on steric hindrance of the glycosyl acceptor. In all cases, we used the diazirine and the phenol in equimolar amounts, so as not to prejudice the relative importance of these partners in ulterior applications.

Results and Discussion. – 1. *Glycosidations with 4-Methoxyphenol, Phenol, and 4-Nitrophenol* (see *Schemes 1* and *2*). Reaction of the D-glucosylidene-derived diazirine **3** with *4-methoxyphenol* in CH_2Cl_2 at r.t. for 7 h gave, after flash chromatography (FC), 69% of a 3:1 mixture[1]) of the β- and α-D-glucosides **4** and **5** and 16% of a 1:1 mixture[2]) of the anomeric *C*-glucosides **6** and **7** (*Scheme 1*). The anomers **4** and **5** were partially separated by FC; their physical data are in agreement with the published ones [6] [7] [9] (see *Exper. Part*). The *C*-glucosides **6** and **7** could not be separated by HPLC. The acetates **8** and **9**,

Scheme 1



a) 1 Equiv. of 4-methoxyphenol, CH_2Cl_2, r.t. 69% of **4**/**5** (3:1) and 16% of **6**/**7** (1:1). b) 1 Equiv. of phenol, CH_2Cl_2, r.t. 70% of **10**/**11** (4:1) and 13% of **12**/**13** (1:1). c) 1 Equiv. of 4-nitrophenol, CH_2Cl_2, r.t., 75% of **14**/**15** (3:2). d) Ac_2O, pyridine, 100%.

[1]) The ratio was determined by anal. HPLC of the crude product and of the mixture after FC (see *Exper. Part*).

[2]) The ratio was determined from the ^{1}H-NMR spectrum of the mixture **6**/**7** and by anal. HPLC of the mixture of the acetylated *C*-glucosides **8** and **9**.

obtained upon acetylation in Ac_2O and pyridine, were partially separated by FC and completely by prep. HPLC. Deacetylation of **8** and **9** gave the pure anomers **6** and **7**, respectively, of which the structure was deduced from spectroscopic data.

The IR spectra of **6** and **7** show an OH absorption at 3400–3390 cm^{-1}. The OH group was evidenced to be phenolic by the bathochromic shift of the absorption at the longest wavelength in the UV spectrum of **6** from 296 nm (EtOH) to 320 nm (0.15M NaOEt in EtOH) upon basification. In the ^{1}H-NMR spectrum of the β-D-anomer **6**, the OH signal is hidden under the *multiplets* of the aromatic H-atoms of the benzyl groups at 7.36–7.22 ppm. The 3 aromatic H-atoms of the aryl substituent at C(1) give rise to a *doublet* at 6.89 (J = 8.8) for H–C(3′), to a *doublet* of *doublets* at 6.83 (J = 3.0, 8.8) for H–C(4′), and to a *doublet* at 6.73 ppm (J = 3.0) for H–C(6′), evidencing the substitution pattern of the aromatic ring. H–C(1) resonates at 4.39 ppm as a *doublet* with $J(1,2)$ = 9.1 Hz. In the ^{1}H-NMR spectrum of the α-D-anomer **7**, the OH signal appears at 7.49 ppm as a *singlet*. The 3 aromatic H-atoms of the aryl residue at C(1) resonate at 7.45 (*d*, J = 2.9, H–C(6′)), 6.84 (*d*, J = 8.8, H–C(3′)), and 6.79 ppm (*dd*, J = 2.9, 8.8, H–C(4′)). The similarity of this coupling pattern with the one of the aryl H-atoms of **6** evidences the same substitution pattern of the C(1) substituent in **6** and **7**. The large down-field shift of H–C(6′) of the α-D-anomer **7** as compared to the chemical shift of H–C(6′) of the β-D-anomer **6** ($\Delta\delta$ = 0.72 ppm) is probably due to anisotropic effects of the phenyl ring of the 2-benzyloxy group. The *doublet* of H–C(1) of **7** occurs at 5.37 ppm ($J(1,2)$ = 5.2 Hz). In the ^{13}C-NMR spectrum of **6**, the *doublet* of C(1) appears at 81.13 ppm[3]), and thus characteristically at a higher field than in the corresponding *O*-glycoside **4** (102.76 ppm). C(3) – resonating at 86.14 ppm – is deshielded. The assignments agree with literature data [15]. It appears that the signal at *ca.* 86 ppm is typical for benzylated β-D-configurated *C*-aryl glucosides. The corresponding signals of **7** are found at 73.36 ppm for C(1) and 81.46 ppm for C(3). Similarly, C(5) of the α-D-anomer **7** resonates at a higher field then C(5) of the β-D-anomer **6** (72.5 *vs.* 78.65 ppm), as expected from a γ-effect.

The regioselectivity of the *C*-glucosidation is derived from the observation of a NOE at H–C(4′) and H–C(6′) upon irradiation of the methoxy H-atoms of **6**. The ^{13}C-NMR spectrum of the corresponding acetate **8**, showing 2 *d* for the aromatic C-atoms at relatively high field (115.00 and 114.61 ppm for C(4′) and C(6′)) is in agreement with the postulated regioselectivity[4]). Similarly, the acetylated α-D-anomer **9** gives rise to 2 *d* at 115.77 and 113.75 ppm for C(4′) and C(6′). This indicates the same regioselectivity as in the β-D-anomer.

The reaction of the diazirine **3** with *phenol* in CH_2Cl_2 at r.t. for 7 h gave 70% of a 4:1 mixture[1]) of the *O*-glucosides **10** and **11** and 13% of a 1:1 mixture[5]) of the β- and α-D-*C*-glucosides **12** and **13** (see *Scheme 1*). The anomers **10** and **11** were separated by prep. HPLC, their physical data are in agreement with the published ones [6] [7] [9] [10] (see *Exper. Part*). The mixture **12**/**13** was not separated.

The mixture **12**/**13** shows an OH absorption at 3390 cm^{-1}. In the ^{1}H-NMR spectrum, the *singlets* of the OH groups occur at 7.87 and 7.77 ppm, respectively. The pattern of the signals of the aromatic H-atoms between 7.0 and 6.8 ppm indicates the *ortho*-substitution of the aryl ring at C(1) (see *Exper. Part*). Again, 1 H-atom of the C(1)-aryl substituent resonates at much lower field (br. *d* at 7.79 ppm, J = 7.8) than the other aryl H-atoms (see above). By analogy to **7**, we presume that this H-atom belongs to the α-D-anomer. The *d* of H–C(1) of the β-D-anomer **12** appears at 4.44 ppm with $J(1,2)$ = 9.1 Hz, H–C(1) of **13** resonates at 5.39 ppm with $J(1,2)$ = 5.1 Hz. In the ^{13}C-NMR spectrum of the mixture, one notes again a *doublet* at 86.05 ppm (C(3) of the β-D-anomer **12**). C(1) of **12** resonates around 81.5 ppm (81.57 or 81.52 ppm). For the α-D-anomer **13**, the *doublet* at 81.33 ppm is attributed to C(3) and a *doublet* around 73 ppm (73.55 or 72.78 ppm) to C(1), in analogy to the data of **7** (see above).

The diazirine **3** reacted with *4-nitrophenol* (CH_2Cl_2, r.t., 5 h) to yield 75% of the 4-nitrophenyl glucosides **14** and **15** in a ratio of 3:2[1]) (see *Scheme 1*). The anomers were completely separated by prep. HPLC. The physical data of **14** and **15** are in agreement with the literature [6–8] (see *Exper. Part*).

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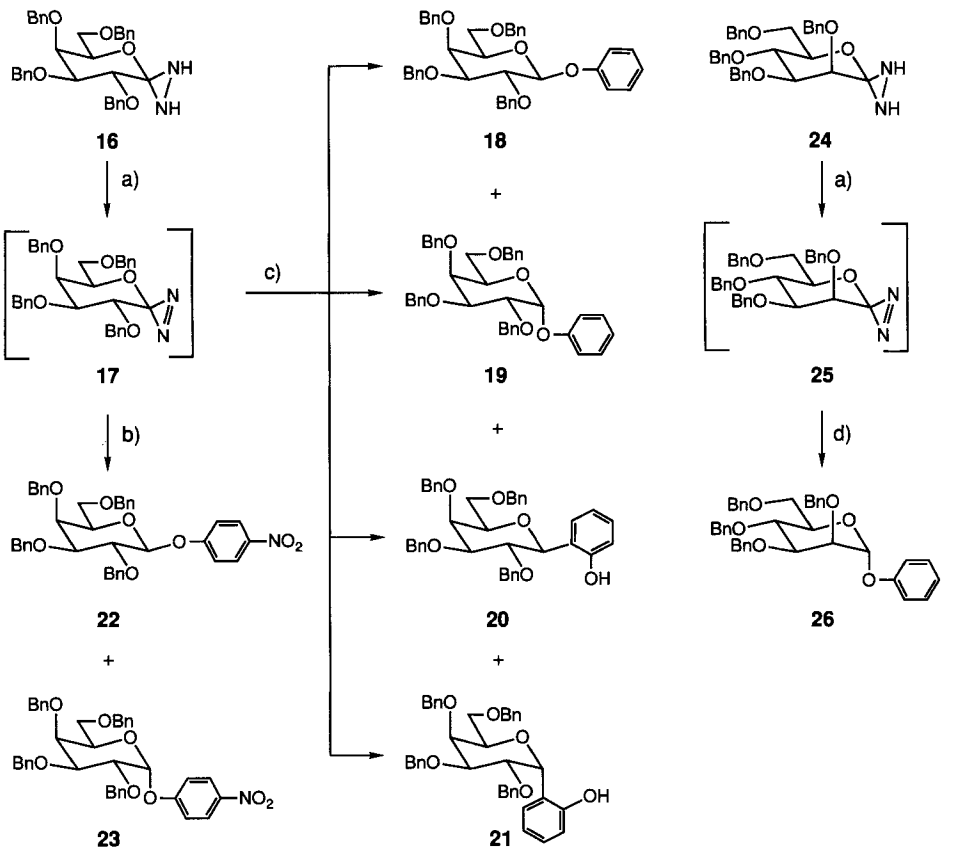
[3]) ^{13}C-NMR chemical shifts were assigned by an inverse ^{1}H,^{13}C-heteronuclear shift correlation experiment.

[4]) For the alternative regioselectivity where the glycosyl residue is *ortho* to the MeO group, only one of the aromatic C-atoms would be expected to resonate below 120 ppm; *cf.* determinations of ^{13}C-NMR chemical shifts of aromatic C-atoms by increment calculations, *e.g.* [16].

[5]) The ratio was determined from the ^{1}H-NMR spectrum of the mixture.

Scheme 2



a) I_2, Et_3N, Et_2O, $-40°$. b) 1 Equiv. of 4-nitrophenol, CH_2Cl_2, r.t., 52% (from **16**) of **22**/**23** (65:35). c) 1 Equiv. of phenol, CH_2Cl_2, r.t., 58% (from **16**) of **18**/**19** (4:1) and 14% of **20**/**21** (1:1). d) 1 Equiv. of phenol, CH_2Cl_2, r.t., 38% (from **24**) of **26**.

To investigate the influence of the configuration at C(4) and at C(2) upon the diastereoselectivity of the glycosidation, we also examined the glycosidation of phenol and 4-nitrophenol with the D-galactosylidene-derived diazirine **17** and of phenol with the D-mannosylidene-derived diazirine **25** (*Scheme 2*). The D-galactosylidene-derived diazirine **17** reacted with phenol (CH_2Cl_2, r.t., 5 h) to yield 58% (from the diaziridine **16**) of a 4:1 mixture[1]) of the β- and α-D-anomers **18** [17] and **19** and 14% of a 1:1 mixture[5]) of the anomeric *C*-galactosides **20** and **21**. The mixture **18**/**19** was separated by FC. The reaction of **17** with 4-nitrophenol in CH_2Cl_2 for 2 h at r.t. gave, after FC, 65% (from the diaziridine **16**) of a 65:35 mixture[1]) of the β- and α-D-galactosides **22** and **23** which were separated by another FC and recrystallization of **22** (see *Exper. Part*). The reaction of the D-mannosylidene-derived diazirine **25** with phenol in CH_2Cl_2 at r.t. afforded predominantly the α-D-anomer **26** [10] ($\alpha/\beta > 20:1$, according to the integrals of the anomeric H-atoms in the ^{1}H-NMR spectrum) in 38% from the diaziridine **24**. The low yield is mainly due to the instability of both the diaziridine and the diazirine in the absence of base.

In the ^{1}H-NMR spectrum of **18**, H–C(1) gives rise to a *doublet* at 4.99 ppm with $J = 7.7$ Hz, and in the spectrum of **19**, H–C(1) resonates at 5.51 ppm ($J = 2.9$ Hz). In the ^{13}C-NMR spectra, C(1) of **18** resonates at 101.86 (*d*) and C(1) of **19** at 96.40 ppm (*d*). The mixture **20**/**21** shows an OH absorption at 3410 cm^{-1} in the IR spectrum. In the ^{1}H-NMR spectrum of the mixture, the OH signal of **20** appears as a *singlet* at 7.55 and the one of **21** at 8.14 ppm. H–C(1) of **20** resonates at 4.37 ($J = 9.6$) and H–C(1) of **21** at 5.10 ppm ($J = 1.6$). In the ^{1}H-NMR spectrum, H–C(1) of **22** resonates at 5.06 ppm ($J = 7.6$) and H–C(1) of **23** at 5.50 ppm ($J = 3.6$). The ^{13}C-NMR chemical shift of C(1) of **22** is 100.98 ppm and the one of C(1) of **23** is 96.50 ppm.

The formation of *C*-glycosides in the glycosidations with phenol and the electron-rich 4-methoxyphenol, but not with 4-nitrophenol, supports the assumption that protonation of the diazirine, the carbene, or of an intermediate diazoether[6]), leading to an ion pair, is the first step to occur. The protonated intermediate reacts with the corresponding phenolate anion to form the *O*- and *C*-glycosides. The fact that no *para*-substituted *C*-glycosides were found in the glycosidation of phenol may be rationalized by assuming the formation of a tight ion-pair intermediate. Partial or complete proton transfer from (acidic) OH compounds is currently accepted as the determining feature of the mechanism of formal O, H insertion into nucleophilic carbenes (see [20] and ref. quoted there). The formation of *C*-glycosides as side-products in the kinetically controlled glycosidation of phenols is well precedented [10] [21][7]).

A competition experiment where **3** was exposed at the same time to 1 equiv. each of 4-nitrophenol and 4-methoxyphenol in CH_2Cl_2 at r.t. for 6 h yielded, after FC, 94.5% of a mixture of the *O*-glycosides **14**, **15**, **4**, and **5** and of the *C*-glycosides **6** and **7**, in a 85:15 ratio of *O*- to *C*-glycosides, according to the weight of the fractions of the *O*- and *C*-glycosides after FC. The 4-nitrophenyl and 4-methoxyphenyl glycosides **14** and **15** and **4** and **5**, respectively, were formed in a ratio of 59:41. The ratio was based on the integrals of the signals of the aromatic H-atoms at 8.18 ppm (for **14** and **15**) and at 6.81 ppm (for **4** and **5**) in the ^{1}H-NMR spectrum of the mixture of the *O*-glycosides. The ratios of the anomers **14** and **15** and of **4** and **5** were virtually the same as in the reactions with only one phenol present. Taking into consideration the formation of the *C*-glycosides **6** and **7** (1:1 according to ^{1}H-NMR), the products derived from 4-methoxyphenol and from 4-nitrophenol were formed in about equal amounts. This lack of selectivity may indicate a relatively high basicity of the intermediate, so that the pK_{HA} differences of 4-methoxyphenol ($pK_{HA}(H_2O) = 10.2$ [23] and 4-nitrophenol (pK_{HA} (H_2O) = 7.2 [23]) do not affect the reaction rate. The amount of *C*-glycosides obtained in this competition experiment (27%) is higher than in the reaction without 4-nitrophenol (16%, see above). It is not clear, at this point, to which extent association of the phenols has a bearing on the reaction (*cf.* [24]).

2. *Reaction of Diazirine* **3** *with Methyl Orsellinate* (**1**; see *Scheme 3*). The intermolecular competition experiment (see above) shows that differences of pK_{HA} values of sufficiently acidic compounds have very little (if any) effect upon the selectivity of the glycosidation for such glycosyl acceptors. This may change for glycosyl acceptors possessing more than one OH group of different *kinetic* acidity, a situation which arises when

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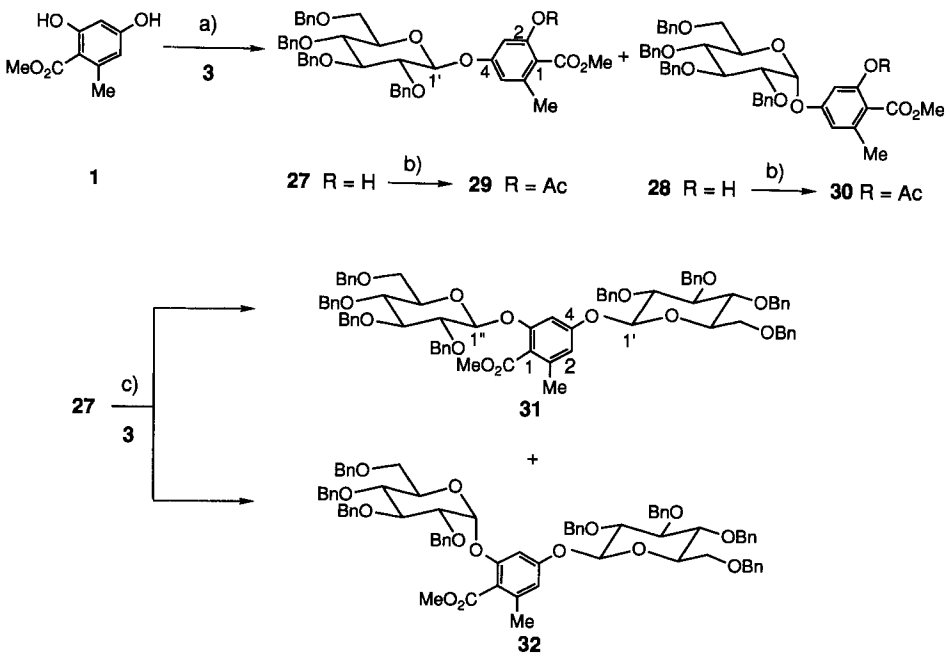
[6]) Although we found no evidence for the formation of diazoethers in the glycosidation of phenols, the *isomerization* of diazirines to diazo compounds has been observed in some cases [18]. Some evidence (UV, IR) indicates the formation of a diazoether in the reaction of **3** with 1,1,1,3,3,3-hexafluoropropan-2-ol [19].

[7]) *C*-Glycosides are the major products when the conditions for the glycosidation of phenols lead to a reversible *O*-glycosidation [22].

Scheme 3



a) 1 Equiv. of methyl orsellinate (**1**), conditions see text. b) Ac_2O, pyridine, 100%. c) 1 Equiv. of **3**, toluene, 40°, 67% of **31**/**32**.

part of the OH groups are chelated, *i.e.* when they function as donors in strong intramolecular H-bonds [25]. An example of such a glycosyl acceptor is methyl orsellinate (**1**) where the OH group in *ortho*-position to the COOMe group is chelated, while the OH group in *para*-position is not.

Reaction of the diazirine **3** with 1 equiv. of methyl orsellinate (**1**) [14] in CH_2Cl_2 at r.t. for 5 h gave 79% of a 66:34 mixture[1]) of the β- and α-D-glucosides **27** and **28**. No 2-*O*-glucosylorsellinate was formed. The mixture **27**/**28** was acetylated in Ac_2O and pyridine to give a mixture **29**/**30** which was separated by MPLC. Each of the anomers **29** and **30** was deacetylated with NaOMe in MeOH to give the pure anomers **27** and **28**, respectively. The solvent dependency of the reaction was studied using nitromethane (r.t., 75% of **27**/**28**, 68:32), dioxane (r.t., 78% of **27**/**28**, 80:20), and toluene (r.t., 78% of **27**/**28**, 85:15). The reaction in toluene was also run at 40° which reduced the reaction time to 45 min, but did not affect the yield and the diastereoselectivity. At 60° in toluene, the reaction was completed after 30 min, yielding 75% of a 85:15 mixture of **27** and **28**. Dioxane and toluene appear to be the solvents of choice for the glycosidation of phenols.

In the IR spectra of **27** and **28** a weak and broad absorption band, starting at 3400 cm^{-1} and being superposed by the C–H vibrations between 3110 and 2870 cm^{-1}, is typical for an OH absorption of a strongly chelated OH group. The stretching vibration of the ester carbonyl bond at 1655 cm^{-1} indicates that the carbonyl O-atom is involved in a H-bond. This is confirmed by the IR spectra of the acetylated glycosides **29** and **30** where the C=O band of the COOMe group appears at much higher wave numbers (1725 cm^{-1}). In the ^{1}H-NMR spectra of **27** and

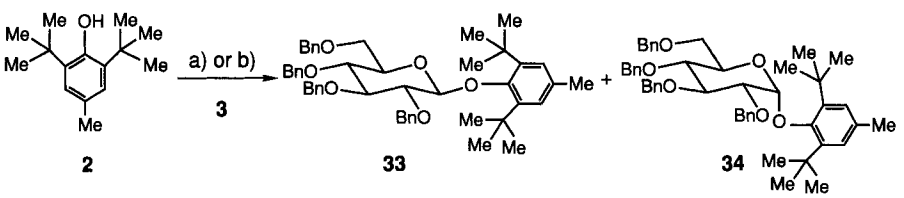
28, the *singlet* of the OH group appears at 11.70 and 11.63 ppm, respectively. H–C(1′) of **27** gives rise to a signal of higher order (*X* part of *ABX* system) at 5.05 ppm. The signal of H–C(1′) of **28** appears as a *d* at 5.49 ppm (J = 3.5 Hz).

The exclusive glycosidation of the OH group of **1** demonstrates that differences in the kinetic acidities of glycosyl acceptors possessing more than one OH group may serve as the basis for a regioselective glycosidation which does not require protective groups. The rate constant for protonation by a chelated OH group is reduced by the stability constant of the H-bond [25]. The difference of the thermodynamic acidities of the OH groups of methyl orsellinate (**1**) is almost certainly unimportant[8]). At this point, one may ask the questions, if the chelated OH group of **1** can be glycosylated at all by **3**, and if the difference in steric hindrance of the two OH groups is relevant. The first question is answered in a positive way by the glycosidation of the protected 4-*O*-glucosylorsellinate **27** with diazirine **3** to give the di-*O*-glucosylated orsellinates **31** and **32** (40°, toluene, 67% of **31**/**32**, 4:3[1])). The second question is answered by the easy glucosidation of 2,6-di(*tert*-butyl)-4-methylphenol (**2**; see below).

The IR spectra of **31** and of **32** show the C=O absorption at 1725 cm^{-1}, typical for the non-chelated COOMe group (see above). In the ^{1}H-NMR spectrum of **31**, the *doublets* of the two anomeric H-atoms occur at 5.10 (J = 7.6 Hz) and 5.08 ppm (J = 7.8 Hz). In the ^{1}H-NMR spectrum of **32**, the anomeric H-atom of the 6-*O*-(α-D-glucopyranosyl) substituent resonates at 5.43 ppm with J = 3.4 Hz, the other anomeric H-atom lies under the benzyl H-atoms at *ca.* 5 ppm.

3. *Reaction of the* D-*Glucosylidene-Derived Diazirine* **3** *with 2,6-Di(*tert*-butyl)-4-methylphenol* (**2**; see *Scheme 4*). The concept of using alkoxycarbenes for the synthesis of glycosides *via* deprotonation of sufficiently acidic glycosyl acceptors (or *via* a very polarized insertion reaction) implies that steric hindrance is relatively unimportant. This assumption was checked by treating diazirine **3** with 1.1 equiv. of the sterically highly hindered 2,6-di(*tert*-butyl)-4-methylphenol (**2**) in CH_2Cl_2 for 7 h at r. t. FC of the product yielded 81% of a 80:20 mixture[1]) of the β- and α-D-glucosides **33** and **34** (see *Scheme 4*) which were separated by MPLC. Carrying out the reaction in toluene at 40° reduced the reaction time to 1 h and afforded 75% of a 84:16 mixture[1]) of **33** and **34**.

Scheme 4



a) 1 Equiv. of **3**, CH_2Cl_2, r. t., 81% of **33**/**34** (80:20). b) 1 Equiv. of **3**, toluene, 40°, 75% of **33**/**34** (84:16).

In the ^{1}H-NMR spectrum of the β-D-glucoside **33**, H–C(1) resonates at 5.17 ppm (*d*, J = 7.8 Hz). In the ^{13}C-NMR spectrum of **33**, the *d* of C(1) occurs at 102.80 ppm. H–C(1) of the α-D-anomer **34** resonates at 5.28 ppm (*d*, J = 2.6 Hz). The relatively small values of J(2,3) and J(3,4) (5.6 and 6.5 Hz resp.) indicate that **34** does not assume a chair conformation. In the ^{13}C-NMR spectrum of **34**, the *doublet* of C(1) – appearing at 100.86 ppm – lies

[8]) The microscopic pK_{HA} values of the *ortho*- and *para*-OH groups of **1** are estimated to be quite similar to each other [26]. The pK_{HA} values of *ortho*-vanilline and of *para*-vanilline are 7.9 and 7.4, respectively [23]. The macroscopic pK_{HA} value of **1** was determined to be 8.7 (in EtOH/H_2O 1:1).

at relatively low field in comparison to other benzylated aryl α-D-glucosides (see [7]). A relatively large chemical-shift value of C(1) is also observed for 2,6-dimethylphenyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside [7], but not for the benzylated 2-(*tert*-butyl)phenyl α-D-glucopyranoside [7]. The $[M]_D$ value of **34** (+264.5°) is small as compared to other aryl α-D-glucosides (see [7]). The benzylated 2,6-dimethylphenyl α-D-glucoside shows the same tendency ([7]: $[M]_D = +297°$, $c = 0.8$), but not the benzylated 2-(*tert*-butyl)phenyl α-D-glucoside ([7]:$[M]_D = +478°$). This may reflect an increasingly stronger deviation of the aryloxy substituent from the axial position. One notes a qualitative correlation between δ(C(1)) and the molecular rotation.

In all cases of the glycosidation of phenols, the 1,2-*trans*-configurated glycosides are the main products. This is not surprising in the case of the D-mannopyranoside **26**, as stereoelectronic and steric factors contribute to the formation of the axial product; an excellent diastereoselectivity ensues. It is, however, rather surprising that the 1,2-*trans*-configurated D-glucosides and D-galactosides, possessing an equatorially oriented phenoxy substituent, are the main products of the glycosidation, since one expects a stereoelectronically preferred axial attack of the phenolate anion on the hypothetical intermediate oxonium ion in the absence of a neighbouring-group participation. As the result of the glycosidation of the D-mannose-derived diazirine **25** shows, the preferred formation of the β-D-glucosides and -galactosides cannot simply be the result of a preferred equatorial attack. Steric approach control might rationalize the results in the D-*manno*-, but hardly in the D-*gluco*- and D-*galacto*-series. The simplest explanation requires that the 2-benzyloxy group participates in the stabilization of an incompletely solvated and thus highly reactive oxonium ion. The postulate of a neighbouring-group participation of the 2-benzyloxy group and the possible role of a diazoether intermediate (diastereoselective *C*-protonation?) is currently being examined.

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Experimental Part

General. After workup, processing of the org. layer as usual implies drying ($MgSO_4$) and evaporation of the solvent at or below 40°. Qual. TLC: 0.25-mm precoated silica-gel plates (*Merck*, Kieselgel *60 F_{254}*) with the solvent systems indicated; detection by spraying the plates with a soln. of 0.02M I_2 and 0.30M KI in 10% aq. H_2SO_4 soln. followed by heating at *ca.* 200°, or – for specific detection of the diazirines – with a 2% soln. of 4-(4-nitrobenzyl)pyridine in acetone and heating at 100° [27], or – for specific detection of phenolic compounds – with the 'fast blue salt B reagent' [28]. Flash chromatography (FC): silica gel *Merck 60* (0.040–0.063 mm). Medium-pressure liquid chromatography (MPLC): silica gel *Merck 60* (0.015–0.040 mm). High-performance liquid chromatography (HPLC): anal. *Spherisorb* silica (5 μm) 250 × 4.6 mm column or *Merck LiChrosorb Si60* 250 × 4.0 mm cartridge; prep. *Spherisorb* silica (5 μm) 250 × 20 mm column. M.p. uncorrected. Optical rotations: 1-dm cell at 25° and 365, 436, 546, 578, and 589 nm; values at 589 nm were determined from a regression curve, unless an ORD effect was noted in which case only the value obtained at 589 nm was considered. UV spectra (λ_{max} in nm (ε)): 1-cm quartz cell. IR spectra: 3% $CHCl_3$ soln. ^1H- and ^{13}C-NMR spectra: chemical shifts in ppm relative to TMS as internal standard.

1. Diazirines 3, 17 and 25 (see [1]). – *1-Azi-2,3,4,6-tetra-O-benzyl-1-deoxy-D-glucopyranose* (**3**). At r.t., the powdered 1-hydrazi-2,3,4,6-tetra-*O*-benzyl-1-deoxy-D-glucopyranose [1] (500 mg, 0.9 mmol) was dissolved in MeOH (25 ml), and Et_3N (2 ml, 14.3 mmol) was added. The soln. was cooled to −45°[9]), and, under efficient stirring, a soln. of I_2 (230 mg, 0.9 mmol) in MeOH (4.5 ml) was added dropwise (0.5 ml/min). After addition of *ca.* $^2/_3$ of the I_2 soln., **3** started to precipitate. After complete addition, the crystalline **3** was filtered off under N_2 and washed with cold (−40°) MeOH and then 3 times with hexane (r.t.). The crystals were dried under high vacuum to give 458 mg (92%) of **3**. Spectroscopic data: see [1].

[9]) When the reaction was performed at higher temperatures (up to 0°), precipitation of **3** was incomplete (see [1]).

For the synthesis of the D-*galacto*- and D-*manno*-derived products (**18**–**23** and **26**, see *Scheme 2*), the diazirines **17** and **25** were prepared directly before use according to [1]. The yields refer to the corresponding diaziridines **16** and **24**, thus are calculated over two steps (see below).

2. Glycosidations. – 2.1. *General Procedure.* Under N_2, a soln. of the diazirine (**3**, **17**, or **25**) in the indicated pre-dried solvent was added to a mixture of the phenol (1.0–1.1 equiv.) and activated powdered molecular sieves (4 Å) in the same solvent, and the mixture was stirred at the temp. indicated. After all diazirine had disappeared, the mixture was filtered through *Celite* and processed as described below for each case. Phenol and 4-methoxyphenol were distilled. Methyl orsellinate (**1**) was prepared according to [14].

2.2. *Reaction of* **3** *with 4-Methoxyphenol.* Reaction of **3** (250 mg, 0.45 mmol) in CH_2Cl_2 (3 ml) with 4-methoxyphenol (57 mg, 0.46 mmol) and molecular sieves (200 mg) in CH_2Cl_2 (2 ml) for 7 h at r.t. gave, after evaporation and FC (hexane/CH_2Cl_2 1:1) of the residue, a 3:1 mixture[1]) **4**/**5** (187 mg, 69%) and a 1:1 mixture[2]) **6**/**7** (43 mg, 16%). For characterization, **4**/**5** was partially separated by another FC (hexane/CH_2Cl_2 2:1). The mixture **6**/**7** was acetylated in Ac_2O/pyridine 1:1 at r.t. for 2 h. Dilution with CH_2Cl_2, extraction with 1M aq. Na_2CO_3 and with H_2O, and processing of the org. layer as usual afforded **8**/**9** which was separated by prep. HPLC (hexane/CH_2Cl_2 1:10, 16 ml/min); partial separation ion was also achieved by FC (hexane/CH_2Cl_2 1:4)).

*4′-Methoxyphenyl 2,3,4,6-Tetra-*O*-benzyl-β-*D*-glucopyranoside* (**4**) [6] [9]: Anal. HPLC (hexane/CH_2Cl_2 1:7, 1.5 ml/min): t_R 5.6 min. R_f (hexane/CH_2Cl_2 1:7) 0.26. M.p. 94.5–95.5° ([6]: 94.5–95.5°) $[\alpha]_D^{25} = -4.0$ ($c = 0.7$, $CHCl_3$; [6]: $[\alpha]_D = -4$). IR: 3090*w*, 3060*w*, 3030*w*, 3000*w*, 2950*w* (sh), 2930*m* (sh), 2910*m*, 2870*m*, 2840*w* (sh), 2060*w*, 1950*w*, 1875*w*, 1810*w*, 1610*w*, 1590*w*, 1495*m*, 1450*m*, 1380*w* (sh), 1355*m*, 1255*m* (sh), 1220*m* (br.), 1145*m* (sh), 1090*s* (sh), 1060*s*, 1030*s*, 1010*s*, 950*w* (sh), 910*w*, 860*w*, 820*m*, 690*m*, 660*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.38–7.27 (*m*, 18 arom. H); 7.21–7.18 (*m*, 2 arom. H); 7.05 (*AA′* of *AA′XX′*, $J_o = 8.9$, $J_m = 6.1$, $J_p = 0.2$, 2 arom. H); 6.82 (*XX′* of *AA′XX′*, 2 arom. H); 5.06 (*d*, $J = 10.9$, PhCH_2); 4.96 (*d*, $J = 10.9$, PhCH_2); 4.89 (*X* of *ABX*, H–C(1)); 4.85 (*d*, $J = 11.1$, PhCH_2); 4.84–4.81 (*m*, 2 H, PhCH_2); 4.61 (*d*, $J = 12.1$, PhCH_2); 4.58 (*d*, $J = 11.1$, PhCH_2); 4.55 (*d*, $J = 12.1$, PhCH_2); 3.80 (*m*, $J = 1.9$, H_A–C(6)); 3.78 (*s*, CH_3O); 3.74–3.64 (*m*, H–C(2), H–C(3), H–C(4), H_B–C(6)); 3.58 (*ddd*, $J = 1.9$, 5.1, 9.4, H–C(5)). ^{13}C-NMR (50 MHz, $CDCl_3$): 155.24, 151.48 (2*s*, C(1′), C(4′)); 138.48 (*s*, arom. C); 138.25 (*s*, arom. C); 138.13 (*s*, arom. C); 137.99 (*s*, arom. C); 128.47–127.51 (*m*, arom. C); 118.39, 114.50 (4*d*, C(2′), C(3′), C(5′), C(6′)); 102.76 (*d*, C(1)); 84.66 (*d*); 82.05 (*d*); 77.73 (*d*); 75.69 (*t*, PhCH_2); 74.97 (*d* + 2*t*, 2 PhCH_2); 73.43 (*t*, PhCH_2); 68.88 (*t*, C(6)); 55.57 (*q*, CH_3O).

*4′-Methoxyphenyl 2,3,4,6-Tetra-*O*-benzyl-α-*D*-glucopyranoside* (**5**) [6] [7] [9]: Anal. HPLC (hexane/CH_2Cl_2 1:7, 1.5 ml/min): t_R 4.6 min. R_f (hexane/CH_2Cl_2 1:7) 0.27. $[\alpha]_D^{25} = +92.1$ ($c = 0.9$, $CHCl_3$; [7]: $[\alpha]_D = +92$). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.40–7.24 (*m*, 18 arom. H); 7.16–7.13 (*m*, 2 arom. H); 7.02 (*AA′* of *AA′XX′*, $J_o = 8.8$, $J_m = 6.1$, $J_p = 0.3$, 2 arom. H); 6.81 (*XX′* of *AA′XX′*, 2 arom. H); 5.36 (*d*, $J = 3.5$, H–C(1)); 5.05 (*d*, $J = 10.8$ PhCH_2); 4.88 (*d*, $J = 10.8$, PhCH_2); 4.86 (*d*, $J = 10.8$, PhCH_2); 4.80 (*d*, $J = 12.0$, PhCH_2); 4.69 (*d*, $J = 12.0$, PhCH_2); 4.59 (*d*, $J = 12.0$, PhCH_2); 4.50 (*d*, $J = 10.8$, PhCH_2); 4.42 (*d*, $J = 12.0$, PhCH_2); 4.19 (*dd* ('*t*'), $J = 9.3$, H–C(3)); 3.93 (*ddd*, $J = 2.0$, 3.3, 9.3, H–C(5)); 3.79–3.71 (*m*, H–C(4), H_A–C(6)); 3.78 (*s*, CH_3O); 3.70 (*dd*, $J = 3.5$, 9.6, H–C(2)); 3.65 (*dd*, $J = 2.0$, 10.7, H_B–C(6)).

*(1S)-1,5-Anhydro-2,3,4,6-tetra-*O*-benzyl-1-*C*-(2′-hydroxy-5′-methoxyphenyl)-*D*-glucitol* (**6**): R_f (hexane/CH_2Cl_2 1:7) 0.17. Anal. HPLC (hexane/CH_2Cl_2 1:7, 1.5 ml/min): t_R 10.3 min. UV (EtOH): 296 ($3.7 \cdot 10^3$), 267 ($1.4 \cdot 10^3$). UV (0.15M NaOEt in EtOH): 320 ($4.5 \cdot 10^3$), 267 ($2.2 \cdot 10^3$). $[\alpha]_D^{25} = +21.5$ ($c = 0.5$, $CHCl_3$). IR: 3390*m* (br.), 3090*w*, 3060*w*, 3030*w*, 3000*w*, 2910*m*, 2870*m*, 1950*w*, 1875*w*, 1810*w*, 1585*w*, 1490*m*, 1465*m*, 1450*m*, 1420*m* (sh), 1350*m*, 1305*m*, 1130*s* (sh), 1085*s* (sh), 1065*s*, 1030*s*, 1000*m* (sh), 810*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.36–7.22 (*m*, 16 arom. H, OH); 7.19–7.16 (*m*, 2 arom. H); 7.04–6.99 (*m*, 2 arom. H); 6.89 (*d*, $J = 8.8$, H–C(3′); NOE on irradiation at 3.68 ppm); 6.83 (*dd*, $J = 3.0$, 8.8, H–C(4′); NOE on irradiation at 3.68 ppm); 6.73 (*d*, $J = 3.0$, H–C(6′)); 4.99 (*d*, $J = 11.1$, PhCH_2); 4.91 (*d*, $J = 11.1$, PhCH_2); 4.86 (*d*, $J = 10.9$, PhCH_2); 4.62 (*d*, $J = 12.1$, PhCH_2); 4.56 (*d*, $J = 10.8$, PhCH_2); 4.49 (*d*, $J = 12.1$, PhCH_2); 4.48 (*d*, $J = 10.0$, PhCH_2); 4.39 (*d*, $J = 9.1$, H–C(1)); 3.90 (*dd*, ('*t*'), $J = 9.1$, 9.4, H–C(4)); 3.83 (*d*, $J = 10.0$, PhCH_2); 3.78 (*dd* ('*t*'), $J = 9.1$, H–C(3)); 3.78 (*dd*, $J = 2.8$, 10.5, H_A–C(6)); 3.73 (*m*, H–C(2)); 3.72 (*dd*, $J = 2.0$, 10.5, H_B–C(6)); 3.68 (*s*, CH_3O); 3.59 (*ddd* ('*dt*'), $J = 2.0$, 2.6, 9.8, H–C(5)). ^{13}C-NMR (100 MHz, $CDCl_3$)[3]): 149.25 (*s*, C(2′), C(5′)); 138.57, 138.03, 137.22 (4*s*, 4 arom. C); 128.51–127.58 (*m*, arom. C); 123.80 (*s*, C(1′)); 118.39 (*d*, C(3′)); 115.58 (*d*, C(4′)); 113.71 (*d*, C(6′)); 86.14 (*d*, C(3)); 81.85 (*d*, C(2)); 81.13 (*d*, C(1)); 78.65 (*d*, C(5)); 77.37 (*d*, C(4)); 75.63 (*t*, PhCH_2); 75.41 (*t*, PhCH_2); 75.24 (*t*, PhCH_2); 73.43 (*t*, PhCH_2); 68.03 (*t*, C(6)); 55.63 (*q*, CH_3O). Anal. calc. for $C_{41}H_{42}O_7$ (646.78): C 76.14, H 6.54; found: C 76.03, H 6.28.

*(1R)-1,5-Anhydro-2,3,4,6-tetra-*O*-benzyl-1-*C*-(2′-hydroxy-5′-methoxyphenyl)-*D*-glucitol* (**7**): R_f (hexane/CH_2Cl_2 1:7) 0.17. Anal. HPLC (hexane/CH_2Cl_2 1:7, 1.5 ml/min): t_R 10.3 min. $[\alpha]_D^{25} = +43.7$ ($c = 0.3$, $CHCl_3$). IR: 3400*m* (br.), 3090*w*, 3060*w*, 3030*w*, 3000*m*, 2910*m*, 2870*m*, 2840*m* (sh), 2800*w* (sh), 1970*w* (sh), 1955*w*, 1875*w*, 1810*w*, 1750*w*, 1620*w* (sh), 1605*w* (sh), 1585*w*, 1490*s*, 1465*m*, 1450*m*, 1355*s*, 1305*m*, 1270*m*, 1230*m*, 1145*s* (sh),

1130*s* (sh), 1110*s* (sh), 1070*s* (sh), 1065*s*, 1040*s* (sh), 1030*s* (sh), 985*m*, 940*w*, 910*m*, 885*w* (sh), 850*w*, 825*w* (sh), 685*w*, 630*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.49 (*s*, exchangeable with D_2O, OH); 7.45 (*d*, J = 2.9, H–C(6′)); 7.36–7.22 (*m*, 18 arom. H); 7.16–7.10 (*m*, 2 arom. H); 6.84 (*d*, J = 8.8, H–C(3′)); 6.79 (*dd*, J = 2.9, 8.8, H–C(4′)); 5.37 (*d*, J = 5.2, H–C(1)); 5.00 (*d*, J = 11.0, PhCH_2); 4.82 (*d*, J = 11.0, PhCH_2); 4.81 (*d*, J = 10.8, PhCH_2); 4.74 (*d*, J = 11.7, PhCH_2); 4.70 (*d*, J = 11.7, PhCH_2); 4.59 (*d*, J = 12.1, PhCH_2); 4.48 (*d*, J = 10.8, PhCH_2); 4.44 (*d*, J = 12.1, PhCH_2); 4.21 (*dd*, J = 8.2, 9.2, H–C(3)); 4.03 (*dd*, J = 5.2, 9.2, H–C(2)); 3.70 (*dd*, J = 8.2, 9.7, H–C(4)); 3.69 (*s*, CH_3O); 3.65 (*dd*, J = 4.6, 10.7, H_A–C(6)); 3.61 (*dd*, J = 2.4, 10.7, H_B–C(6)); 3.57 (*ddd*, J = 2.4, 4,6, 9.7, H–C(5)). ^{13}C-NMR (50 MHz, $CDCl_3$)[3]: 152.71, 150.30 (2*s*, C(2′), C(5′)); 138.32, 137.89, 137.61 (4*s*, 4 arom. C); 128.56–127.43 (*m*, arom. C); 121.92 (*s*, C(1′)); 117.83 (*d*, C(3′)); 114.84 (*d*, C(4′)); 114.62 (*d*, C(6′)); 81.46 (*d*, C(3)); 80.37 (*d*, C(2)); 77.92 (*d*, C(4)); 75.22 (*t*, PhCH_2); 74.90 (*t*, PhCH_2); 73.36 (*d* and *t*, C(1), PhCH_2); 73.25 (*t*, PhCH_2); 72.75 (*d*, C(5)); 68.71 (*t*, C(6)); 55.67 (*q*, CH_3O).

*(1S)-1-C-(2′-Acetoxy-5′-methoxyphenyl)-1,5-anhydro-2,3,4,6-tetra-*O*-benzyl-*D*-glucitol* (**8**): R_f (hexane/CH_2Cl_2 1:7) 0.10. Anal. HPLC (hexane/CH_2Cl_2 1:10, 1.5 ml/min): t_R 8.5 min. IR: 3090*w*, 3060*w*, 3040*w*, 3000*w*, 2910*m*, 2870*m*, 1970*w* (sh), 1950*w*, 1875*w*, 1810*w*, 1760*s*, 1605*m*, 1590*w* (sh), 1490*m*, 1450*m*, 1360*m*, 1305*w*, 1275*m* (sh), 1260*m*, 1175*m*, 1090*s*, 1070*s*, 1040*s*, 1025*s*, 1010*s*, 940*w*, 900*m*, 855*w*, 690*m*, 600*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.35–7.15 (*m*, 18 arom. H); 7.02 (*X* of *ABX*, H–C(3′)); 6.96–6.92 (*m*, 2 arom. H); 6.91–6.87 (*AB* of *ABX*, H–C(4′), H–C(5′)); 4.94 (*d*, J = 10.9, PhCH_2); 4.90 (*d*, J = 10.7, PhCH_2); 4.89 (*d*, J = 10.9, PhCH_2); 4.68 (*d*, J = 10.7, PhCH_2); 4.59 (*d*, J = 12.0, PhCH_2); 4.51 (*d*, J = 12.0, PhCH_2); 4.43 (*d*, J = 10.5, PhCH_2); 4.27 (*d*, J = 9.3, H–C(1)); 3.99 (*d*, J = 10.5, PhCH_2); 3.86–3.75 (*m*, H–C(2), H–C(3), H–C(4), H_A–C(6)); 3.74 (*s*, CH_3O); 3.72 (*dd*, J = 1.8, 10.6, H_B–C(6)); 3.51 (*ddd*, J = 1.8, 3.1, 9.4, H–C(5)); 2.18 (*s*, CH_3CO). ^{13}C-NMR (50 MHz, $CDCl_3$): 169.87 (*s*, CO); 157.11 (*s*, C(5′)); 142.60 (*s*, C(2′)); 138.58 (*s*, arom. C); 138.25 (*s*, arom. C); 138.08 (*s*, arom. C); 137.65 (*s*, arom. C); 131.29 (*s*, C(1′)); 128.54–127.34 (*m*, arom. C); 124.33 (*d*, C(3′)); 115.00, 114.61 (2*d*, C(4′), C(6′)); 86.88 (*d*); 81.85 (*d*); 79.30 (2*d*); 78.01 (*d*); 75.77 (*t*, PhCH_2); 75.08 (*t*, PhCH_2); 74.69 (*t*, PhCH_2); 73.46 (*t*, PhCH_2); 68.91 (*t*, C(6)); 55.54 (*q*, CH_3O); 20.99 (*q*, CH_3CO).

*(1R)-1-C-(2′-Acetoxy-5′-methoxyphenyl)-1,5-anhydro-2,3,4,6-tetra-*O*-benzyl-*D*-glucitol* (**9**): R_f (hexane/CH_2Cl_2 1:7) 0.13. Anal. HPLC (hexane/CH_2Cl_2 1:10, 1.5 ml/min): t_R 6.0 min. IR: 3090*w*, 3060*w*, 3030*w*, 3000*w*, 2920*m*, 2860*m*, 1970*w* (sh), 1950*w*, 1875*w*, 1810*w*, 1755*s*, 1605*w*, 1590*w*, 1560*w*, 1490*m*, 1450*m*, 1420*w*, 1360*m*, 1305*w*, 1275*w*, 1170*m* (sh), 1145*m* (sh), 1115*s*, 1080*s* (sh), 1070*s*, 1045*s* (sh), 1030*m*, 1010*s*, 910*m*, 865*w*, 835*w*, 690*w*, 640*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.49 (*d*, J = 3.0, H–C(6′)); 7.34–7.23 (*m*, 16 arom. H); 7.19–7.15 (*m*, 4 arom. H); 6.94 (*d*, J = 8.8, H–C(3′)); 6.84 (*dd*, J = 3.0, 8.8, H–C(4′)); 5.27 (*d*, J = 4.8, H–C(1)); 4.82 (*d*, J = 11.2, PhCH_2); 4.75 (*d*, J = 11.1, PhCH_2); 4.71 (*d*, J = 11.2, PhCH_2); 4.58 (*d*, J = 12.1, PhCH_2); 4.53 (*d*, J = 11.1, PhCH_2); 4.51 (*d*, J = 11.8, PhCH_2); 4.48 (*d*, J = 11.8, PhCH_2); 4.46 (*d*, J = 12.1, PhCH_2); 4.12 (*dd* ('*t*'), J = 7.2, H–C(3)); 3.96 (*dd*, J = 4.8, 7.2, H–C(2)); 3.84 (*dd*, J = 7.2, 9.2, H–C(4)); 3.73 (*s*, CH_3O); 3.69 (*dd*, J = 3.2, 10.6, H_A–C(6)); 3.59–3.53 (*m*, H–C(5), H_B–C(6)); 2.14 (*s*, CH_3CO). ^{13}C-NMR (50 MHz, $CDCl_3$): 169.85 (*s*, CO); 156.67 (*s*, C(5′)); 142.60 (*s*, C(2′)); 138.33 (*s*, 2 arom. C); 138.12 (*s*, arom. C); 138.03 (*s*, arom. C); 130.61 (*s*, C(1′)); 128.34–127.35 (*m*, arom. C); 123.38 (*d*, C(3′)); 115.77, 113.75 (2*d*, C(4′), C(6′)); 81.52 (*d*); 79.10 (*d*); 77.30 (*d*); 74.00 (*t*, PhCH_2); 73.89 (*t*, PhCH_2); 73.53 (*t*, PhCH_2); 73.05 (*d*); 72.94 (*t*, PhCH_2); 69.80 (*d*); 68.83 (*t*, C(6)); 55.48 (*q*, CH_3O); 20.81 (*q*, CH_3CO).

2.3. *Reaction of* **3** *with Phenol.* Reaction of **3** (205 mg, 0.37 mmol) in CH_2Cl_2 (2 ml) with phenol (35 mg, 0.37 mmol) and molecular sieves (100 mg) in CH_2Cl_2 (1 ml) for 7 h at r.t. yielded, after evaporation and FC (hexane/CH_2Cl_2 1:1) of the residue, a 4:1 mixture[1]) **10**/**11** (159 mg, 70%) which had been separated by prep. HPLC (hexane/AcOEt 10:1, 16 ml/min) and a 1:1 mixture[5]) of **12**/**13** (30 mg, 13%).

*Phenyl 2,3,4,6-Tetra-*O*-benzyl-β-*D*-glucopyranoside* (**10**) [6] [9] [10]: R_f (hexane/CH_2Cl_2 1:7) 0.42. M.p. 81° ([6]: 80–81°). $[\alpha]_D^{25} = -11.8$ (c = 1.2, $CHCl_3$); [6]: $[\alpha]_D = -12$). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.37–7.26 (*m*, 20 arom. H); 7.22–7.19 (*m*, 2 arom. H); 7.11–7.04 (*m*, 3 arom. H); 5.07 (*d*, J = 10.9, PhCH_2); 5.03 (*X* of *ABX*, H–C(1)); 4.97 (*d*, J = 10.9, PhCH_2); 4.88–4.82 (*m*, 3 PhCH_2); 4.61 (*d*, J = 12.0, PhCH_2); 4.59 (*d*, J = 10.8, PhCH_2); 4.54 (*d*, J = 12.0, PhCH_2); 3.81 (*dd*, J = 1.8, 10.8, H_A–C(6)); 3.78–3.75 (*m*, 2 H); 3.73–3.67 (*m*, 2 H); 3.63 (*ddd*, J = 1.7, 5.0, 9.4, H–C(5)). ^{13}C-NMR (50 MHz, $CDCl_3$); 157.57 (*s*, C(1′)); 138.40 (*s*, arom. C); 138.31 (*s*, arom. C); 138.21 (*s*, arom. C); 129.68 (*d*, 2 arom. C); 128.70–127.73 (*m*, arom. C); 122.82 (*d*, C(4′)); 117.08 (*d*, C(2′), C(6′)); 101.87 (*d*, C(1)); 84.86 (*d*); 82.19 (*d*); 80.85 (*d*); 77.90 (*t*, PhCH_2); 75.92 (*d*); 75.19 (*t*, 2 PhCH_2); 73.66 (*t*, PhCH_2); 69.05 (*t*, C(6)).

*(1S)- and (1R)-1,5-Anhydro-1-C-(2′-hydroxyphenyl)-2,3,4,6-tetra-*O*-benzyl-*D*-glucitol* (**12** and **13**, resp.). R_f (hexane/CH_2Cl_2 1:7) 0.21. IR: 3390*m* (br.), 3090*w*, 3060*w*, 3030*w*, 3000*w*, 2910*m*, 2870*m*, 1950*w*, 1875*w*, 1810*w*, 1615*w*, 1580*m* (sh), 1485*m*, 1465*m* (sh), 1450*m*, 1360*m*, 1310*m*, 1270*m*, 1125*s* (sh), 1085*s*, 1065*s*, 1030*s*, 990*m*, 945*w*, 910*w*, 870*w*, 860*w*, 835*w*, 690*w*, 630*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.87 (*s*, exchangeable with D_2O, OH); 7.79 (br., *d*, J = 7.8, H–C(6′)); 7.77 (*s*, exchangeable with D_2O, OH); 7.36–7.16 (*m*, 39 arom. H); 7.13–7.10 (*m*, 2 arom. H); 7.02–6.99 (*m*, 2 arom. H); 6.96 (*dd*, J = 1.0, 8.2, H–C(3′)); 6.92 (*dd*, J = 1.0, 7.7, H–C(3′)); 6.91 (*dt*, J = 1.1, 7.3, H–C(5′)); 6.86 (*dt*, J = 1.1, 7.5, H–C(5′)); 5.39 (*d*, J = 5.1, H–C(1), **13**); 5.00–4.47 (13 *d*, PhCH_2); 4.45 (*d*,

J = 12.1, PhCH_2); 4.44 (*d*, J = 9.1, H–C(1), **12**); 4.40 (*d*, J = 10.0, PhCH_2); 4.20 (*dd* ('*t*'), J = 8.2, 9.0, H–C(3), **13**); 4.03 (*dd*, J = 5.1, 9.0, H–C(2), **13**); 3.92 (*dd*, ('*t*'), J = 9.2, H–C(4), **12**); 3.80–3.57 (*m*, 9 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 156.59, 155.58 (2*s*, 2 C(2')); 138.54 (*s*); 138.32 (*s*); 137.98 (*s*); 137.90 (*s*); 137.81 (*s*); 137.63 (2*s*); 129.70, 129.60, 129.20, 129.02 (4*d*, 2 C(4'), 2 C(6')); 128.48–126.72 (*m*, arom. C); 123.02, 121.29 (2*s*, 2 C(1')); 119.85, 119.75, 117.58, 117.29 (4*d*, 2 C(3'), 2 C(5')); 86.05 (*d*); 81.57 (*d*); 81.52 (*d*); 81.33 (*d*); 80.45 (*d*); 78.57 (*d*); 77.85 (*d*); 77.28 (*d*); 75.61 (*t*, PhCH_2); 75.24 (*t*, 2 PhCH_2); 75.12 (*t*, PhCH_2); 74.83 (*t*, PhCH_2); 73.55 (*d*); 73.39 (*t*, 2 PhCH_2); 73.28 (*t*, PhCH_2); 72.78 (*d*); 68.68, 67.92 (2*t*, 2 C(6)).

2.4. *Reaction of* **3** *with 4-Nitrophenol.* Diazirine **3** (320 mg, 0.58 mmol) in CH_2Cl_2 (2 ml) was treated with 4-nitrophenol (81 mg, 0.58 mmol) and molecular sieves (200 mg) in CH_2Cl_2 (5 ml) for 5 h at r.t. The filtrate was extracted with 1N aq. NaOH and H_2O and the org. layer processed as usual to give, after FC (hexane/CH_2Cl_2 1:2) of the residue, a 3:2 mixture[1]) **14**/**15** (290 mg, 75%) which was separated by prep. HPLC (hexane/AcOEt 5:1, 16 ml/min).

*4'-Nitrophenyl 2,3,4,6-Tetra-*O*-benzyl-β-*D*-glucopyranoside* (**14**) [6] [8]: Anal. HPLC (hexane/AcOEt 4:1, 1.5 ml/min): t_R 4.4 min. Anal. HPLC (hexane/CH_2Cl_2 1:7, 1.5 ml/min): t_R 4.4 min. M.p. 113–114° ([6]: 112.5–114°). $[\alpha]_D^{25} = -35.3$ (c = 0.4, $CHCl_3$; [8]: $[\alpha]_D = -33.5$). IR: 3090*w*, 3060*w*, 3030*w*, 3000*w*, 2950*w* (sh), 2920*m*, 2860*m*, 1950*w*, 1870*w*, 1810*w*, 1730*w*, 1610*w*, 1595*m*, 1495*m*, 1455*w*, 1345*s*, 1300*w*, 1240*m*, 1145*m*, 1110*s* (sh), 1070*s*, 1025*m*, 1005*m* (sh), 920*w*, 860*m*, 845*w*, 690*w*, 660*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.18 (*AA'* of *AA'XX'*, J_o = 9.1, J_m = 5.2, J_p = 0.2, H–C(3'), H–C(5')); 7.35–7.26 (*m*, 18 arom. H); 7.21–7.18 (*m*, 2 arom. H); 7.09 (*XX'* of *AA'XX'*, H–C(2'), H–C(6')); 5.09 (*X* of *ABX*, H–C(1)); 4.96 (*d*, J = 11.0, PhCH_2); 4.95 (*d*, J = 10.9, PhCH_2); 4.86 (*d*, J = 10.8, PhCH_2); 4.86 (*d*, J = 10.9, PhCH_2); 4.85 (*d*, J = 11.0, PhCH_2); 4.59–4.55 (*m*, PhCH_2); 4.51 (*d*, J = 11.9, PhCH_2); 3.82–3.73 (*m*, 3 H); 3.71–3.62 (*m*, 3 H).

*4'-Nitrophenyl 2,3,4,6-Tetra-*O*-benzyl-α-*D*-glucopyranoside* (**15**) [6] [7]: Anal. HPLC (hexane/AcOEt 4:1, 1.5 ml/min): t_R 5.0 min. Anal. HPLC (hexane/CH_2Cl_2 1:7, 1.5 ml/min): t_R 3.7 min. $[\alpha]_D^{25} = +131.2$ (c = 0.3, $CHCl_3$; [7]: $[\alpha]_D = +131$). IR: 3090*w*, 3070*w*, 3030*w*, 3000*w*, 2920*m*, 2870*m*, 1955*w*, 1870*w*, 1810*w*, 1610*w*, 1595*m*, 1515*w*, 1495*m*, 1455*w*, 1345*s*, 1300*w*, 1145*m*, 1130*m* (sh), 1110*s* (sh), 1095*s*, 1085*s*, 1070*s*, 1040*s* (sh), 1030*s*, 1005*m*, 910*w*, 870*m*, 850*w*, 690*w*, 660*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.18 (*AA'* of *AA'XX'*, H–C(3'), H–C(5')); 7.41–7.24 (*m*, 18 arom. H); 7.15–7.08 (*m*, 4 arom. H); 5.45 (*d*, J = 3.5, H–C(1)); 5.05 (*d*, J = 10.8, PhCH_2); 4.91 (*d*, J = 10.8, PhCH_2); 4.86 (*d*, J = 10.7, PhCH_2); 4.85 (*d*, J = 12.1, PhCH_2); 4.64 (*d*, J = 12.1, PhCH_2); 4.57 (*d*, J = 12.0, PhCH_2); 4.49 (*d*, J = 10.7, PhCH_2); 4.41 (*d*, J = 12.0, PhCH_2); 4.18 (*dd*, ('*t*'), J = 8.3, 9.4, H–C(3)); 3.80 (*dd*, J = 8.3, 10.0, H–C(4)); 3.80–3.65 (*m*, H–C(5)); 3.75 (*dd*, J = 3.5, 9.6, H–C(2)); 3.70 (*dd*, J = 3.1, 10.6, H_A–C(6)); 3.54 (*dd*, J = 1.5, 10.6, H_B–C(6)).

2.5. *Competition Experiment.* Reaction of **3** (100 mg, 0.18 mmol) in CH_2Cl_2 (0.7 ml) with a mixture of 4-methoxyphenol (23 mg, 0.185 mmol) and 4-nitrophenol (25.8 mg, 0.185 mmol) and molecular sieves (100 mg) in CH_2Cl_2 (2.5 ml) for 6 h yielded, after extraction (1M aq. Na_2CO_3 and H_2O) and processing of the org. layer as usual, 120 mg of crude product. FC (hexane/CH_2Cl_2 1:2) gave 95 mg of a 59:41 mixture of **14**/**15** and **4**/**5** and 17 mg of a 1:1 mixture **6**/**7**. The mixtures were characterized by the HPLC retention times of their components and by their ^{1}H-NMR spectra (see *General Part*).

2.6. *Reaction of* **17** *with Phenol.* A soln. of **17** (freshly prepared from **16** (300 mg, 0.54 mmol) according to [1]) in CH_2Cl_2 (3 ml) was added to a stirred mixture of phenol (55 mg, 0.58 mmol) and molecular sieves (150 mg) in CH_2Cl_2 (1 ml); the mixture was stirred at r.t. for 2.5 h, filtered through *Celite* and evaporated. FC (hexane/AcOEt 10:1) gave a 4:1 mixture[1]) **18**/**19** (194 mg, 58% from **16**) and a 1:1 mixture[5]) **21**/**22** (47 mg, 145 from **16**). The anomers **18** and **19** were separated by another FC (hexane/AcOEt 20:1).

*Phenyl 2,3,4,6-Tetra-*O*-benzyl-β-*D*-galactopyranoside* (**18**). R_f (hexane/CH_2Cl_2 1:7) 0.40. M.p. 61° ([17]: 61–62°). $[\alpha]_D^{25} = -17.0$ (c = 1.1, $CHCl_3$; [17]: $[\alpha]_D = -18.4$). IR: 3090*w*, 3060*m*, 3030*m*, 3000*m*, 2920*m*, 2870*s*, 2810*w*, 1970*w* (sh), 1955*w*, 1875*w*, 1810*w*, 1600*m*, 1590*m*, 1490*m*, 1450*m*, 1380*m*, 1360*m*, 1350*m* (sh), 1300*m*, 1290*m*, 1255*m*, 1230*m*, 1150*s*, 1110*s*, 1070*s*, 1025*s*, 1000*s*, 945*w*, 910*m*, 890*w*, 865*w*, 810*m*, 690*m*, 665*m* (sh), 640*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.40–7.23 (*m*, 22 arom. H); 7.10–7.04 (*m*, H–C(2'), H–C(4'), H–C(6')); 5.02 (*d*, J = 10.8, PhCH_2); 4.99 (*d*, J = 7.7, H–C(1)); 4.99 (*d*, J = 11.1, PhCH_2); 4.87 (*d*, J = 10.8, PhCH_2); 4.80 (*d*, J = 11.8, PhCH_2); 4.75 (*d*, J = 11.8, PhCH_2); 4.66 (*d*, J = 11.7, PhCH_2); 4.47 (*d*, J = 11.6, PhCH_2); 4.41 (*d*, J = 11.6, PhCH_2); 4.13 (*dd*, J = 7.7, 9.8, H–C(2)); 3.96 (*d*, J = 2.7, H–C(4)); 3.71 (*m*, H–C(5)); 3.69–3.60 (*m*, H–C(3), CH_2(6)). ^{13}C-NMR (50 MHz, $CDCl_3$): 157.39 (*s*, C(1')); 138.43 (*s*, 2 arom. C); 138.29 (*s*, arom. C); 137.80 (*s*, arom. C); 129.27 (*d*, C(3'), C(5')); 128.26–127.41 (*m*, arom. C); 122.33 (*d*, C(4')); 116.83 (*d*, C(2'), C(6')); 101.86 (*d*, C(1)); 81.99 (*d*); 79.10 (*d*); 75.23 (*t*, PhCH_2); 74.42 (*t*, PhCH_2); 73.74 (*d*); 73.44 (*t*, PhCH_2); 73.32 (*d*); 72.92 (*t*, PhCH_2); 68.79 (*t*, C(6)).

*Phenyl 2,3,4,6-Tetra-*O*-benzyl-α-*D*-galactopyranoside* (**19**). $[\alpha]_D^{25} = +78$ (c = 1.0, $CHCl_3$). IR: 3090*w*, 3070*w*, 3020*w* (sh), 3010*m*, 2930*m*, 2870*m*, 1955*w* (sh), 1880*w* (br.), 1820*w* (br.), 1600*m*, 1590*w*, 1455*m*, 1370*w* (sh), 1355*m*

(sh), 1350*m*, 1290*w*, 1260*w*, 1230*m* (br.), 1170*w* (sh), 1155*m* (sh), 1150*m*, 1130*s*, 1100*s*, 1080*s* (sh), 1055*s*, 1040*s*, 1030*s*, 1005*m*, 990*m*, 910*w*, 890*w*, 870*w*, 860*w*, 820*w*, 690*m*, 665*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.45–7.16 (*m*, 22 arom. H); 7.11–6.98 (*m*, H–C(2′), H–C(4′), H–C(6′)); 5.51 (*d*, *J* = 2.9, H–C(1)); 4.98 (*d*, *J* = 11.4, PhC*H*$_2$); 4.91 (*d*, *J* = 11.7, PhC*H*$_2$); 4.84 (*d*, *J* = 12.0, PhC*H*$_2$); 4.80 (*d*, *J* = 11.7, PhC*H*$_2$); 4.70 (*d*, *J* = 12.0, PhC*H*$_2$); 4.59 (*d*, *J* = 11.3, PhC*H*$_2$); 4.40 (*d*, *J* = 11.6, PhC*H*$_2$); 4.32 (*d*, *J* = 11.6, PhC*H*$_2$); 4.22–4.06 (*m*, H–C(2), H–C(3), H–C(4), H–C(5)); 3.59 (*dd*, *J* = 7.2, 9.3, H$_A$–C(6)); 3.48 (*dd*, *J* = 5.8, 9.3, H$_B$–C(6)).

*(1*S*)- and (1*R*)-1,5-Anhydro-2,3,4,6-tetra-*O*-benzyl-*1-C-*(2′-hydroxyphenyl)*-*D*-galactitol* (**20** and **21**, resp.). R_f (hexane/CH_2Cl_2 1:7) 0.31. IR: 3410*m*, 3090*w*, 3070*w*, 3040*w*, 3000*m*, 2920*m*, 2880*m*, 1950*w*, 1875*w*, 1810*w*, 1720*w*, 1615*w* (sh), 1585*w*, 1485*w*, 1450*m*, 1360*m*, 1305*w*, 1230*m* (br.), 1085*s* (br.), 1025*s*, 905*m*, 870*w*, 690*m*, 660*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): signals of **20**: 7.56 (*s*, exchangeable with D_2O, OH); 7.40–7.21 (*m*, 19 arom. H); 7.18 (*dd*, *J* = 1.7, 7.5, H–C(6′)); 7.06–7.02 (*m*, 2 arom. H); 6.94 (*dd*, *J* = 1.1, 8.1, H–C(3′)); 6.88 (*d*, *J* = 1.1, 7.4, H–C(5′)); 5.08 (*d*, *J* = 11.8, PhC*H*$_2$); 4.78 (*s*, 2 H, PhC*H*$_2$); 4.69 (*d*, *J* = 11.8, PhC*H*$_2$); 4.48 (*d*, *J* = 10.0, PhC*H*$_2$); 4.46 (*d*, *J* = 11.8, PhC*H*$_2$); 4.40 (*d*, *J* = 11.8, PhC*H*$_2$); 4.37 (*d*, *J* = 9.6, H–C(1)); 4.22 (*dd* (*t*′), *J* = 9.5, H–C(2)); 3.90 (br., *d*, *J* = 2.2, H–C(4)); 3.87 (*d*, *J* = 10.0, PhC*H*$_2$); 3.72–3.67 (*m*, H–C(5)); 3.69 (*dd*, *J* = 2.5, 9.4, H–C(3)); 3.62–3.55 (*m*, CH_2(6)); signals of **21**: 8.14 (*s*, exchangeable with D_2O, OH); 7.40–7.21 (*m*, 19 arom. H); 7.18 (*dd*, H–C(6′)); 7.07–7.04 (*m*, 2 arom. H); 6.90 (*dd*, *J* = 1.2, 8.1, H–C(3′)); 6.78 (*d*, *J* = 1.2, 7.5, H–C(5′)); 5.10 (*d*, *J* = 1.6, H–C(1)); 4.71 (*d*, *J* = 12.0, PhC*H*$_2$); 4.58–4.33 (several *d*, PhC*H*$_2$); 4.25–4.21 (*m*, 2 H); 4.13 (*dd*, *J* = 3.0, 5.6, 1 H); 3.87 (*m*, 1 H); 3.77–3.74 (*m*, 2 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 157.18, 155.75 (2*s*, 2 C(2′)); 138.44 (*s*); 138.36 (*s*); 138.30 (*s*); 138.23 (*s*); 138.05 (*s*); 137.71 (*s*); 137.63 (*s*); 137.45 (*s*); 129.87, 129.76, 129.53, 129.36 (4*d*, 2 C(4′), 2 C(6′)); 129.10–127.39 (*m*, arom. C); 123.58, 121.78 (2*s*, 2 C(1′)); 119.49 (*d*); 119.07 (*d*); 117.21 (2*d*); 83.59 (*d*); 82.16 (*d*); 78.43 (*d*); 77.05 (*d*); 75.52 (*t*, PhC*H*$_2$); 74.89 (*d*); 74.78 (*d*); 74.42 (*t*, PhC*H*$_2$); 73.58 (*d*, *t*); 73.37 (*t*, PhC*H*$_2$); 73.33 (*t*, PhC*H*$_2$); 73.28 (*d*); 72.99 (*t*, PhC*H*$_2$); 72.55 (*t*, PhC*H*$_2$); 72.20 (*t*, PhC*H*$_2$); 71.96 (*d*); 68.46, 65.30 (2*t*, 2 C(6)). Anal. calc. for $C_{40}H_{40}O_6$ (616.75): C 77.90, H 6.54; found: C 77.81, H 6.57.

2.7. *Reaction of* **17** *with 4-Nitrophenol.* A soln. of **17** (freshly prepared from **16** (500 mg, 0.90 mmol) according to [1]) in CH_2Cl_2 (5 ml) was added to a mixture of 4-nitrophenol (126 mg, 0.91 mmol) and molecular sieves (250 mg) in CH_2Cl_2 (5 ml). After stirring for 2 h at r.t., the mixture was filtered through *Celite* and extracted with 2N aq. NaOH and H_2O. Processing of the org. layer as usual and FC (hexane/AcOEt 4:1) of the residue gave a 65:35 mixture **22**/**23** (389 mg, 65%) which was separated by another FC to give **22** (204 mg, 34%, after recrystallization from Et_2O/hexane) and **23** (115 mg, 19%).

*4′-Nitrophenyl 2,3,4,6-Tetra-*O*-benzyl-β-*D*-*galactopyranoside (**22**). M.p. 124°. $[\alpha]_D^{25} = -43.8$ (*c* = 1.1, $CHCl_3$). IR: 3110*w*, 3080*w*, 3060*w*, 3030*w*, 3000*w*, 2910*w*, 2910*w*, 2870*m*, 1950*w*, 1870*w*, 1810*w*, 1605*w* (sh), 1590*m*, 1510*m*, 1490*m*, 1470*w* (sh), 1450*w*, 1340*s*, 1295*w*, 1095*s*, 1060*s*, 1025*m*, 990*m*, 940*w*, 910*w*, 860*m*, 845*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.14 (*AA′* of *AA′XX′*, H–C(3′), H–C(5′)); 7.39–7.24 (*m*, 20 arom. H); 7.08 (*XX′* of *AA′XX′*, H–C(2′), H–C(6′)); 5.06 (*dd*, *J* = 7.6, H–C(1)); 4.98 (*d*, *J* = 11.6, PhC*H*$_2$); 4.92 (*d*, *J* = 11.0, PhC*H*$_2$); 4.88 (*d*, *J* = 11.0, PhC*H*$_2$); 4.79 (*d*, PhC*H*$_2$); 4.76 (*d*, PhC*H*$_2$); 4.65 (*d*, *J* = 11.6, PhC*H*$_2$); 4.47 (*d*, *J* = 11.7, PhC*H*$_2$); 4.42 (*d*, *J* = 11.7, PhC*H*$_2$); 4.16 (*dd*, *J* = 7.6, 9.7, H–C(2)); 3.96 (br. *d*, *J* = 2.5, H–C(4)); 3.73 (br., *dd*, *J* = 6.3, 6.8, H–C(5)); 3.65 (*dd*, *J* = 2.5, 9.7, H–C(3)); 3.64 (*dd*, *J* = 6.6, 9.5, H$_A$–C(6)); 3.46 (*dd*, *J* = 6.3, 9.5, H$_B$–C(6)). ^{13}C-NMR (50 MHz, $CDCl_3$): 161.99 (*s*, C(1′)); 142.63 (*s*, C(4′)); 138.22 (*s*, arom. C); 138.12 (*s*, arom. C); 138.07 (*s*, arom. C); 137.66 (*s*, arom. C); 128.84–127.59 (*m*, arom. C); 125.68 (*d*, C(3′), C(5′)); 116.54 (*d*, C(2′), C(6′)); 100.98 (*d*, C(1)); 81.98 (*d*); 78.79 (*d*); 75.58 (*t*, PhC*H*$_2$); 74.61 (*t*); 74.35 (*d*); 73.68 (*t*, PhC*H*$_2$); 73.12 (*d*, *t*); 68.86 (*t*, C(6)). Anal. calc. for $C_{40}H_{39}NO_8$ (660.75): C 72.60, H 5.94, N 2.12; found: C 72.53, H 6.06, N 1.89.

*4′-Nitrophenyl 2,3,4,6-Tetra-*O*-benzyl-α-*D*-galactopyranoside* (**23**). $[\alpha]_D^{25} = +80.9$ (*c* = 1.3, $CHCl_3$). IR: 3110*w*, 3080*w*, 3060*w*, 3030*w*, 3000*w*, 2950*m* (sh), 2920*m*, 2870*m*, 1950*w*, 1870*w*, 1810*w*, 1605*m* (sh), 1590*s*, 1510*m*, 1490*m*, 1450*m*, 1340*s*, 1295*w*, 1090*s* (br.), 1070*s*, 1035*s*, 1025*s*, 1010*s* (sh), 905*m*, 865*m*, 845*m*, 690*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.16 (*AA′* of *AA′XX′*, H–C(3′), H–C(5′)); 7.45–7.23 (*m*, 18 arom. H); 7.17–7.15 (*m*, 2 arom. H); 7.12 (*XX′* of *AA′XX′*, H–C(2′), H–C(6′)); 5.50 (*d*, *J* = 3.6, H–C(1)); 4.99 (*d*, *J* = 11.3, PhC*H*$_2$); 4.91 (*d*, *J* = 11.6, PhC*H*$_2$); 4.89 (*d*, *J* = 11.9, PhC*H*$_2$); 4.82 (*d*, *J* = 11.6, PhC*H*$_2$); 4.68 (*d*, *J* = 12.0, PhC*H*$_2$); 4.59 (*d*, *J* = 11.3, PhC*H*$_2$); 4.37 (*d*, *J* = 11.5, PhC*H*$_2$); 4.32 (*d*, *J* = 11.5, PhC*H*$_2$); 4.23 (*dd*, *J* = 3.6, 10.0, H–C(2)); 4.12 (*dd*, *J* = 2.8, 10.0, H–C(3)); 4.05 (*dd*, *J* = 0.9, 2.8, H–C(4)); 3.95 (br. *t*, *J* = 6.0, 7.0, H–C(5)); 3.54 (*dd*, *J* = 7.0, 9.3, H$_A$–C(6)); 3.46 (*dd*, *J* = 6.0, 9.3, H$_B$–C(6)). ^{13}C-NMR (50 MHz, $CDCl_3$): 161.91 (*s*, C(1′)); 142.51 (*s*, C(4′)); 138.50 (*s*, arom. C); 138.36 (*s*, arom. C); 138.12 (*s*, arom. C); 137.64 (*s*, arom. C); 128.60–127.36 (*m*, arom. C); 125.65 (*d*, C(3′), C(5′)); 116.73 (*d*, C(2′), C(6′)); 96.50 (*d*, C(1)); 78.70 (*d*); 82.05 (*d*); 82.05 (*d*); 75.99 (*d*); 74.97 (*t*, PhC*H*$_2$); 74.63 (*d*); 73.90 (*t*, PhC*H*$_2$); 73.39 (*t*, PhC*H*$_2$); 73.29 (*t*, PhC*H*$_2$); 70.77 (*d*); 68.53 (*t*, C(6)).

2.8. *Reaction of* **25** *with Phenol.* A soln. of **25** (prepared from **24** (200 mg, 0.36 mmol) according to [1]) in CH_2Cl_2 (2 ml) was added to a mixture of phenol (35 mg, 0.37 mmol) and molecular sieves (100 mg) in CH_2Cl_2 (1 ml). The mixture was stirred at r.t. for 2 h, then filtered through *Celite* and evaporated to give, after FC, *phenyl*

*2,3,4,6-tetra-*O*-benzyl-α-*D*-mannopyranoside* (**26**) [10]: 85 mg, 38%. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.42–7.24 (*m*, 20 arom. H); 7.20–7.17 (*m*, 2 arom. H); 7.06–6.77 (*m*, 3 arom. H); 5.61 (*d*, *J* = 1.9, H–C(1)); 4.92 (*d*, *J* = 10.7, PhCH_2); 4.82 (*d*, *J* = 12.4, PhCH_2); 4.78 (*d*, *J* = 12.5, PhCH_2); 4.73 (*d*, *J* = 11.7, PhCH_2); 4.69 (*d*, *J* = 11.7, PhCH_2); 4.66 (*d*, *J* = 12.0, PhCH_2); 4.55 (*d*, *J* = 10.7, PhCH_2); 4.46 (*d*, *J* = 12.0, PhCH_2); 4.18–4.11 (*m*, H–C(3), H–C(4)); 3.98 (*dd*, ('*t*'), *J* = 9.2, H–C(2)); 3.90–3.87 (*m*, H–C(5)); 3.81 (*dd*, *J* = 4.5, 10.9, H_A–C(6)); 3.69 (*dd*, *J* = 1.8, 10.9, H_B–C(6)).

2.9. *Reactions of* **3** *with Methyl 2,4-Dihydroxy-6-methylbenzoate* (= *Methyl Orsellinate*; **1**). Reaction of **3** (500 mg, 0.91 mmol) in CH_2Cl_2 (4 ml) with **1** (170 mg, 0.93 mmol) and molecular sieves (200 mg) in CH_2Cl_2 (4 ml) for 7.5 h at r.t. afforded, after evaporation and FC (hexane/CH_2Cl_2 1:2) of the residue, a 66:34 mixture[1]) **27**/**28** (507 mg, 79%). This mixture was stirred in Ac_2O (2 ml) and pyridine (2 ml) for 1 h at r.t., then diluted with CH_2Cl_2 and washed with 1M aq. $NaHCO_3$ and H_2O. The org. layer was processed as usual to give quantitatively a mixture **29**/**30** which was separated by MPLC (hexane/CH_2Cl_2 1:7). The acetates **29** and **30** were each deacetylated by treatment with a soln. of NaOMe in MeOH at r.t., followed by neutralization with 1N HCl under cooling, extraction with CH_2Cl_2 and processing of the org. layer as usual. After FC (hexane/CH_2Cl_2 1:1), pure **27** and **28** (each 100%) resp., were obtained and crystallized from Et_2O/hexane.

*Methyl 2-Hydroxy-6-methyl-4-[(2′,3′,4′,6′-tetra-*O*-benzyl-β-*D*-glucopyranosyl)oxy]benzoate* (**27**): Anal. HPLC (hexane/CH_2Cl_2 1:7, 1.5 ml/min): t_R 6.6 min. R_f (hexane/CH_2Cl_2 1:7) 0.24. M.p. 105–106°. $[\alpha]_D^{25} = -25.6$ (*c* = 0.9, $CHCl_3$). IR: 3400–2600*w* (br.), 3110*w* (sh), 3090*w*, 3060*m*, 3030*m*, 3000*m*, 2950*m*, 2910*m*, 2870*m*, 1970*w* (sh), 1950*w*, 1875*w*, 1810*w*, 1725*w*, 1655*s*, 1610*s*, 1580*s*, 1560*w* (sh), 1490*m*, 1485*w*, 1445*m*, 1420*m* (sh), 1375*m* (sh), 1360*m*, 1320*s*, 1255*s*, 1200*s*, 1175*s*, 1135*s* (sh), 1070*s*, 1025*m*, 995*m*, 950*w*, 905*w*, 800–720*m* (br.), 660*w*, 645*w*, 625*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 11.70 (*s*, exchangeable with D_2O, OH–C(2)); 7.34–7.25 (*m*, 18 arom. H); 7.19–7.16 (*m*, 2 arom. H); 6.51 (*d*, *J* = 2.5, H–C(5)); 6.40 (*dd*, *J* = 2.5, 0.6, H–C(3)); 5.05 (*X* of *ABX*, H–C(1′)); 4.97 (*d*, *J* = 11.0, PhCH_2); 4.94 (*d*, *J* = 12.1, PhCH_2); 4.84 (*d*, *J* = 10.8, PhCH_2); 4.82 (*d*, *J* = 10.4, PhCH_2); 4.80 (*d*, *J* = 10.8, PhCH_2); 4.60 (*d*, *J* = 12.1, PhCH_2); 4.56 (*d*, *J* = 10.8, PhCH_2); 4.51 (*d*, *J* = 12.1, PhCH_2); 3.95 (*s*, CH_3O); 3.79 (*dd*, *J* = 1.9, 10.8, H_A–C(6′)); 3.75–3.68 (*m*, H–C(2′), H–C(3′), H–C(4′), H_B–C(6′)); 3.64–3.61 (*m*, H–C(5′)); 2.49 (*s*, CH_3Ar). ^{13}C-NMR (50 MHz, $CDCl_3$): 171.72 (*s*, CO); 164.99, 161.05 (2*s*, C(4), C(2)); 143.13 (*s*, C(6)); 138.29 (*s*, arom. C); 137.92 (*s*, 3 arom. C); 128.84–127.33 (*m*, arom. C); 111.99 (*d*, C(5)); 106.68 (*s*, C(1)); 101.74 (*d*, C(3)); 100.25 (*d*, C(1′)); 84.35 (*d*); 81.57 (*d*); 77.29 (*d*); 75.47 (*t*, PhCH$_2$); 75.01 (*d*); 74.76 (*t*, 2 PhCH$_2$); 73.24 (*t*, PhCH$_2$); 68.41 (*t*, C(6′)); 51.60 (*q*, CH_3O); 24.19 (*q*, CH_3Ar). Anal. calc. for $C_{43}H_{44}O_9$ (704.82): C 73.28, H 6.29; found: C 73.14, H 6.34.

*Methyl 2-Hydroxy-6-methyl-4-[(2′,3′,4′,6′-tetra-*O*-benzyl-α-*D*-glucopyranosyl)oxy]benzoate* (**28**): Anal. HPLC (hexane/CH_2Cl_2 1:7, 1.5 ml/min): t_R 6.0 min. R_f (hexane/CH_2Cl_2 1:7) 0.24. M.p. 117–118°. $[\alpha]_D^{25} = +127.2$ (*c* = 1.0, $CHCl_3$). IR: 3400–2600*w* (br.), 3110*w* (sh), 3090*w*, 3070*w*, 3040*w*, 3000*w*, 2920*m*, 2870*m*, 1950*w*, 1875*w*, 1810*w*, 1725*w*, 1655*s*, 1615*s*, 1580*m*, 1560*w* (sh), 1490*w*, 1445*m*, 1420*m* (sh), 1375*m* (sh), 1360*m*, 1320*s*, 1255*s*, 1200*s*, 1160*s*, 1130*s*, 1070*s*, 1095*s* (br.), 1065*s*, 1040*s*, 1030*s*, 1005*s*, 995*m*, 910*w*, 845*w*, 690*w*, 660*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 11.63 (*s*, exchangeable with D_2O, OH–C(2)); 7.39–7.22 (*m*, 18 arom. H); 7.15–7.12 (*m*, 2 arom. H); 6.55 (*d*, *J* = 2.5, H–C(5)); 6.45 (br. *d*, *J* = 2.5, H–C(3)); 5.49 (*d*, *J* = 3.5, H–C(1′)); 5.04 (*d*, *J* = 10.8, PhCH_2); 4.88 (*d*, *J* = 11.4, PhCH_2); 4.85 (*d*, *J* = 11.4, PhCH_2); 4.79 (*d*, *J* = 12.1, PhCH_2); 4.65 (*d*, *J* = 12.1, PhCH_2); 4.60 (*d*, *J* = 12.0, PhCH_2); 4.50 (*d*, *J* = 10.8, PhCH_2); 4.41 (*d*, *J* = 12.0, PhCH_2); 4.16 (*m*, H–C(3′)); 3.93 (*s*, CH_3O); 3.79–3.76 (*m*, H–C(4′), H–C(5′)); 3.73–3.68 (*m*, H–C(2′), H_A–C(6′)); 3.56 (br. *d*, *J* = 9.8, H_B–C(6′)); 2.48 (*s*, CH_3Ar). ^{13}C-NMR (50 MHz, $CDCl_3$): 172.01 (*s*, CO); 165.08, 160.69 (2*s*, C(4), C(2)); 143.20 (*s*, C(6)); 138.67, 138.08, 137.81, 137.69 (4*s*, 4 arom. C); 128.67–127.62 (*m*, arom. C); 112.38 (*d*, C(5)); 106.63 (*s*, C(1)); 101.79 (*d*, C(3)); 94.76 (*d*, C(1′)); 81.81 (*d*); 79.37 (*d*); 77.10 (*d*); 75.77 (*t*, PhCH$_2$); 75.13 (*t*, PhCH$_2$); 73.40 (*t*, 2 PhCH$_2$); 71.17 (*d*); 67.96 (*t*, C(6′)); 51.88 (*q*, CH_3O); 24.20 (*q*, CH_3Ar).

*Methyl 2-Acetoxy-6-methyl-4-[(2′,3′,4′,6′-tetra-*O*-benzyl-β-*D*-glucopyranosyl)oxy]benzoate* (**29**): R_f (hexane/CH_2Cl_2 1:7) 0.07. IR: 3090*w*, 3060*w*, 3030*w*, 3000*w*, 2950*m*, 2910*m*, 2870*m*, 2810*w*, 1970*w* (sh), 1955*w*, 1875*w*, 1765*s*, 1725*s*, 1610*s*, 1580*w*, 1560*w* (sh), 1540*w* (sh), 1490*w* (br.), 1450*m*, 1435*m*, 1365*m*, 1305*m*, 1270*s*, 1190*m*, 1135*s*, 1070*s* (br.), 1025*s*, 1010*m*, 955*m*, 910*w*, 890*m*, 820*w*, 690*m*, 660*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.47–7.25 (*m*, 18 arom. H); 7.20–7.16 (*m*, 2 arom. H); 6.78 (*d*, *J* = 2.2, H–C(5)); 6.64 (*d*, *J* = 2.2, H–C(3)); 5.01 (*X* of *ABX*, H–C(1′)); 4.95 (*d*, *J* = 11.0, PhCH_2); 4.93 (*d*, *J* = 10.9, PhCH_2); 4.86–4.78 (*m*, 2 H, PhCH_2); 4.78 (*d*, *J* = 11.0, PhCH_2); 4.58 (*d*, *J* = 12.0, PhCH_2); 4.56 (*d*, *J* = 10.9, PhCH_2); 4.49 (*d*, *J* = 12.0, PhCH_2); 3.86 (*s*, CH_3O); 3.78–3.63 (*m*, H–C(2′), H–C(3′), H–C(4′), H–C(5′), CH_2(6′)); 2.36 (*s*, CH_3Ar); 2.23 (*s*, CH_3CO). ^{13}C-NMR (50 MHz, $CDCl_3$): 168.86 (*s*, CO); 166.30 (*s*, CO); 158.53 (*s*, C(4)); 150.11 (*s*, C(2)); 140.42 (*s*, C(6)); 138.26 (*s*, arom. C); 137.89 (*s*, arom. C); 137.84 (*s*, 2 arom C); 128.26–127.46 (*m*, arom. C); 119.93 (*s*, C(1)); 116.45 (*d*, C(5)); 108.99 (*d*, C(3)); 100.92 (*d*, C(1′)); 84.38 (*d*); 81.70 (*d*); 77.35 (*d*); 75.60 (*t*, PhCH$_2$); 75.09 (*d*); 74.94 (*t*, PhCH$_2$); 74.85 (*t*, PhCH$_2$); 73.37 (*t*, PhCH$_2$); 68.60 (*t*, C(6′)); 51.87 (*q*, CH_3O); 20.83 (*q*, CH_3); 20.67 (*q*, CH_3).

*Methyl 2-Acetoxy-6-methyl-4-[(2′,3′,4′,6′-tetra-*O*-benzyl-α-*D*-glucopyranosyl)oxy]benzoate* (**30**): R_f (hexane/CH_2Cl_2 1:7) 0.10. IR: 3090*w*, 3060*w*, 3030*w*, 3000*w*, 2950*m*, 2920*m*, 2870*m*, 2800*w* (sh), 1970*w* (sh), 1955*w*, 1875*w*, 1765*m*, 1725*s*, 1610*m*, 1575*w*, 1560*w* (sh), 1540*w* (sh), 1490*w* (br.), 1450*m*, 1435*m*, 1365*m*, 1305*m*, 1260*s*, 1190*m*, 1150*s*, 1125*s*, 1090*s* (br.), 1070*s*, 1055*s*, 1040*s*, 1025*s*, 1005*s*, 960*m*, 910*w* (sh), 890*w*, 865*m*, 690*m*, 660*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.46–7.24 (*m*, 18 arom. H); 7.13–7.09 (*m*, 2 arom. H); 6.82 (*d*, J = 2.1, H–C(5)); 6.68 (*d*, J = 2.1, H–C(3)); 5.42 (*d*, J = 3.5, H–C(1′)); 5.03 (*d*, J = 10.8, PhCH_2); 4.87 (*d*, J = 10.5, PhCH_2); 4.85 (*d*, J = 10.5 PhCH_2); 4.79 (*d*, J = 12.1, PhCH_2); 4.46 (*d*, J = 10.8, PhCH_2); 4.38 (*d*, J = 12.1, PhCH_2); 4.63 (*d*, J = 10.6, PhCH_2); 4.60 (*d*, J = 10.6, PhCH_2); 4.14 (*dd*(‘*t*’), J = 8.9, H–C(3′)); 3.86 (*s*, CH_3O); 3.82–3.76 (*m*, H–C(4′), H–C(5′)); 3.72–3.67 (*m*, H–C(2′), H_A–C(6′)); 3.55 (br. *d*, J = 9.8, H_B–C(6′)); 2.38 (*s*, CH_3Ar); 2.26 (*s*, CH_3CO). ^{13}C-NMR (50 MHz, $CDCl_3$): 169.01 (*s*, CO); 166.49 (*s*, CO); 158.02 (*s*, C(4)); 150.15 (*s*, C(2)); 140.40 (*s*, C(6)); 138.63 (*s*, arom. C); 138.03 (*s*, arom. C); 137.74 (*s*, arom. C); 137.61 (*s*, arom. C); 128.51–127.30 (*m*, arom. C); 119.66 (*s*, C(1)); 116.42 (*d*, C(5)); 108.77 (*d*, C(3)); 95.21 (*d*, C(1′)); 81.76 (*d*); 79.41 (*d*); 77.00 (*d*); 75.77 (*t*, PhCH_2); 75.11 (*t*, PhCH_2); 73.45 (*t*, PhCH_2); 73.36 (*t*, PhCH_2); 71.04 (*d*); 67.91 (*t*, C(6′)); 51.99 (*q*, CH_3O); 20.85 (*q*, CH_3); 20.77 (*q*, CH_3).

2.10. *Reaction of* **3** *with* **27**. Reaction of **3** (58 mg, 0.105 mmol) in toluene (0.6 ml) with **27** (72 mg, 0.102 mmol) in toluene (0.6 ml) at 60° for 90 min yielded, after FC (hexane/CH_2Cl_2 1:4), **31** (45.1 mg, 34.9%), **32** (42 mg, 32.5%), and **27** (20.6 mg, 28.6%).

*Methyl 2-Methyl-4,6-bis[(2′,3′,4′,6′-tetra-*O*-benzyl-β-*D*-glucopyranosyl)oxy]benzoate* (**31**): R_f (hexane/CH_2Cl_2 1:7) 0.18. IR: 3090*w*, 3060*w*, 3030*w*, 2980*m*, 2960*m*, 2940*m* (sh), 2910*m*, 2870*m*, 2080*w*, 1950*w*, 1880*w*, 1810*w*, 1725*s*, 1605*w*, 1585*w*, 1445*m*, 1370*s*, 1360*m* (sh), 1300*m*, 1250–1200*s* (br.), 1070*s* (br.), 1000*w*, 940*w*, 910*w*, 850*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.36–7.32 (*m*, 2 arom. H); 7.32–7.18 (*m*, 34 arom. H); 7.14–7.08 (*m*, 4 arom. H); 6.72 (*d*, J = 2.0, H–C(3)); 6.56 (*d*, J = 1.6, H–C(5)); 5.10 (*d*, J = 7.6, 5.08 *d*, J = 7.8, H–C(1′), H–C(1″)); 4.98 (*d*, J = 10.8, PhCH_2); 4.97 (*d*, J = 11.1, PhCH_2); 4.86 (*d*, J = 11.0, PhCH_2); 4.85 (*d*, J = 10.9, PhCH_2); 4.80 (*d*, J = 10.7, PhCH_2); 4.78 (*d*, J = 10.6, PhCH_2); 4.76 (*d*, J = 11.1, PhCH_2); 4.71 (*d*, J = 10.9, PhCH_2); 4.71 (*d*, J = 11.0, PhCH_2); 4.66 (*d*, J = 10.8, PhCH_2); 4.60–4.46 (*m*, 6 H, PhCH_2); 3.76 (*s*, CH_3O); 3.75–3.49 (*m*, 12 H); 2.29 (*s*, CH_3Ar).

*Methyl 2-Methyl-6-[(2′,3′,4′,6′-tetra-*O*-benzyl-α-*D*-glucopyranosyl)oxy]-4-[(2″,3″,4″,6″-tetra-*O*-benzyl-β-*D*-glucopyranosyl)oxy]benzoate* (**32**): R_f (hexane/CH_2Cl_2 1:7) 0.11. IR: 3090*w*, 3060*w*, 3040*w*, 3000*w*, 2920*m*, 2860*m*, 1950*w*, 1875*w*, 1810*w*, 1720*m*, 1600*m*, 1590*m* (sh), 1450*m*, 1435*m* (sh), 1355*m*, 1305*m* (sh), 1260*m*, 1030*s* (sh), 1070*s* (br.), 1030*s*, 955*w*, 910*w*, 850*w*, 690*w*, 660*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.35–7.17 (*m*, 38 arom. H); 7.15–7.10 (*m*, 2 arom. H); 6.74 (*d*, J = 2.0, H–C(3)); 6.59 (*d*, J = 1.7, H–C(5)); 5.43 (*d*, J = 3.4, H–C(1″)); 4.98 (*d*, H–C(1′)); 4.97 (*d*, J = 10.9, PhCH_2); 4.95 (*d*, J = 11.3, PhCH_2); 4.93 (*d*, J = 11.5, PhCH_2); 4.86–4.75 (*m*, 6 H, PhCH_2); 4.67 (*d*, J = 11.9, PhCH_2); 4.62 (*d*, J = 11.9, PhCH_2); 4.57 (2*d*, J = 11.5, 2 PhCH_2); 4.50 (*d*, J = 11.8, PhCH_2); 4.47 (*d*, J = 10.5, PhCH_2); 4.46 (*d*, J = 12.1, PhCH_2); 4.25 (*d*, J = 12.0, PhCH_2); 4.03 (*dd*(‘*t*’), J = 9.2, H–C(3″)); 3.86 (*m*, H–C(5″)); 3.78 (*m*, H–C(4″)); 3.78 (*s*, CH_3O); 3.75–3.65 (H_A–C(6″), H–C(2′), H–C(3′), H–C(4′), CH_2(6′)); 3.64 (*dd*, J = 3.4, 9.7, H–C(2″)); 3.57 (*m*, H–C(5′)); 3.43 (*dd*, J = 1.6, 10.7, H_B–C(6″)); 2.27 (*s*, CH_3Ar).

2.11. *Reactions of* **3** *with 2,6-Di*(tert-*butyl*)*-4-methylphenol* (**2**). 2.11.1. Reaction of **3** (300 mg, 0.54 mmol) in toluene (4 ml) with **2** (132 mg, 0.60 mmol) and molecular sieves (200 mg) in toluene (3 ml) at 40° for 1 h afforded, after evaporation and FC (hexane/CH_2Cl_2 3:1) of the residue, a 84:16 mixture[1]) **33**/**34** (304 mg, 75%) which was separated by MPLC (hexane/CH_2Cl_2 2:1).

2.11.2. Reaction of **3** (200 mg, 0.36 mmol) in CH_2Cl_2 (3 ml) with **2** (88 mg, 0.40 mmol) and molecular sieves (100 mg) in CH_2Cl_2 (2 ml) at r. t. for 7 h yielded, after evaporation and FC (hexane/CH_2Cl_2 3:1) of the residue, a 80:20 mixture[1]) **33**/**34** (219 mg, 81%).

2′,6′-Di(tert-*butyl*)*-4′-methylphenyl 2,3,4,6-Tetra-*O*-benzyl-β-*D*-glucopyranoside* (**33**): Anal. HPLC (hexane/CH_2Cl_2 1:1, 1.0 ml/min): t_R 5.7 min. R_f (hexane/CH_2Cl_2 1:2) 0.42. $[\alpha]_D^{25}$ = +20.5 (c = 0.6, $CHCl_3$). IR: 3090*w*, 3070*w*, 3030*w*, 3000*m*, 2960*m*, 2910*m*, 2870*m*, 1955*w*, 1880*w*, 1810*w*, 1750*w*, 1600*w*, 1590*w* (sh), 1495*w*, 1485*w*, 1455*m*, 1435*w*, 1425*w*, 1395*w*, 1375*m*, 1360*m*, 1320*w*, 1275*w*, 1185*w*, 1155*m*, 1150*m*, 1110*s*, 1070*s*, 1030*m*, 990*w*, 965*w* (sh), 950*w* (sh), 910*w*, 885*w*, 865*w*, 690*w*, 660*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.41–7.37 (*m*, 2 arom. H); 7.35–7.23 (*m*, 14 arom. H); 7.20–7.17 (*m*, 2 arom. H); 7.13–7.09 (*m*, 2 arom. H); 7.00 (*AB*, 2 arom. H); 5.20 (*d*, J = 11.8, PhCH_2); 5.17 (*d*, J = 7.8, H–C(1)); 4.98 (*d*, J = 10.8, PhCH_2); 4.83 (*d*, J = 10.8, PhCH_2); 4.81 (*d*, J = 11.8, PhCH_2); 4.54 (*d*, J = 10.8, PhCH_2); 4.08 (*d*, J = 11.8, PhCH_2); 4.02 (*d*, J = 11.8, PhCH_2); 3.87 (*dd*, J = 7.8, 9.2, H–C(2)); 3.74 (*dd*(‘*t*’), J = 8.8, 9.1, H–C(3)); 3.67 (*dd*, J = 1.4, 11.5, H_A–C(6)); 3.52 (*dd*, J = 8.8, 9.8, H–C(4)); 3.45 (*dd*, J = 5.5, 11.5, H_B–C(6)); 3.32 (*ddd*, J = 1.4, 5.5, 9.8, H–C(5)); 2.10 (*s*, CH_3Ar); 1.47 (*s*, 2 $(CH_3)_3$C). ^{13}C-NMR (50 MHz, $CDCl_3$): 149.80 (*s*, C(1′)); 138.57 (*s*); 138.52 (*s*); 138.31 (*s*); 138.05 (*s*); 131.73 (*s*);

128.33–127.32 (*m*); 102.80 (*d*, C(1)); 85.00 (*d*); 83.13 (*d*); 78.26 (*d*); 76.48 (*d*); 75.95 (*t*, PhCH$_2$); 75.17 (*t*, PhCH$_2$); 74.98 (*t*, PhCH$_2$); 73.14 (*t*, PhCH$_2$); 68.97 (*t*, C(6)); 35.75 (*s*, 2 C, $(CH_3)_3C$); 32.64 (*q*, 6 C, $(CH_3)_3C$); 21.04 (*q*, CH_3Ar). Anal. calc. for $C_{49}H_{58}O_6$ (742.99): C 79.21, H 7.87; found: C 79.15, H 7.80.

2′,6′-Di(tert-*butyl*)-*4′-methylphenyl 2,3,4,6-Tetra*-O-*benzyl*-α-D-*glucopyranoside* (**34**). Anal. HPLC (hexane/CH_2Cl_2 1:1, 1.0 ml/min): t_R 5.0 min. R_f (hexane/CH_2Cl_2 1:2) 0.49. $[\alpha]_D^{25} = +35.6$ ($c = 0.16$, $CHCl_3$). IR: 3090*w*, 3060*w*, 3030*w*, 3000*w*, 2950*s*, 2920*m*, 2870*m*, 1950*w*, 1870*w*, 1810*w*, 1720*w*, 1590*w*, 1490*w*, 1480*w*, 1450*m*, 1420*w*, 1390*w*, 1360*m*, 1250*w*, 1140*m* (sh), 1095*s*, 1070*s*, 1040*s* (sh), 1025*s*, 1000*m*, 910*w*, 880*w*, 860*w*, 690*w*, 660*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.35–7.15 (*m*, 20 arom. H); 7.00 (*AB*, 2 arom. H); 5.28 (*d*, $J = 2.6$, H–C(1)); 4.69 (*d*, $J = 11.4$, PhCH_2); 4.62 (*d*, $J = 11.4$, PhCH_2); 4.64–4.54 (*m*, 2 H, PhCH_2); 4.54 (*d*, $J = 11.2$, PhCH_2); 4.51 (*d*, $J = 11.3$, PhCH_2); 4.33 (*d*, $J = 12.3$, PhCH_2); 4.28 (*d*, $J = 12.3$, PhCH_2); 4.18 (*ddd*, $J = 2.4, 3.0, 9.6$, H–C(5)); 4.03 (*dd*, $J = 5.6, 6.5$, H–C(3)); 3.93 (*dd*, $J = 2.6, 5.6$, H–C(2)); 3.75 (*dd*, $J = 6.5, 9.6$, H–C(4)); 3.62 (*dd*, $J = 3.2, 11.1$, H_A–C(6)); 3.54 (*dd*, $J = 2.4, 11.1$, H_B–C(6)); 2.25 (*s*, CH_3Ar); 1.41 (*s*, 2 $(CH_3)_3C$). ^{13}C-NMR (50 MHz, $CDCl_3$): 153.67 (*s*, C(1′)); 142.48 (*s*, 2 arom. C); 138.43 (*s*, 2 arom. C); 138.29 (*s*); 138.20 (*s*); 130.62 (*s*); 128.33–127.32 (*m*); 100.86 (*d*, C(1)); 81.97 (*d*); 78.87 (*d*); 76.80 (*d*); 73.66–73.61 (*d*, *t*); 73.26 (*t*, PhCH_2); 73.23 (*t*, PhCH_2); 73.50 (*t*, PhCH_2); 68.67 (*t*, C(6)); 36.15 (*s*, 2 C, $(CH_3)_3C$); 32.73 (*q*, 6 C, $(CH_3)_3C$); 21.02 (*q*, CH_3Ar).

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